EXHIBIT D

ANALYTICAL METHODS FOR SEMIVOLATILES

Exhibit D - Analytical Methods for Semivolatiles

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1.0 SCOPE AND APPLICATION

1.1 The analytical method that follows is designed to analyze water, soil, sediment, other solid matrices and oily sludges from hazardous waste sites for the organic compounds on the Target Compound List (Exhibit C, SVOA TCL).

1.1.2 The target compound list may be designated as all compounds listed in Exhibit C, SVOA TCL or a subset of those compounds and will be indicated on the chain of custody accompanying each sample delivery group (SDG),

1.2 The method is based on EPA Method 625 (Base/Neutrals and Acids) and it covers the determination of a number of organic compounds that are partitioned into an organic solvent and are amenable to gas chromatography. These target compounds and the contract required quantitation limits (CRQLs) are listed in Exhibit C.

1.3 The method involves solvent extraction of the matrix sample, characterization to determine the appropriate analytical protocol to be used followed by appropriate cleanup procedure and GC/MS analysis to determine the semivolatile organic compounds present in the sample.

1.4 Problems have been associated with the following compounds analyzed by this method:

1.4.1 Dichlorobenzidine and 4-chloroaniline can be subject to oxidative losses during solvent concentration.

1.4.2 Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reactions in acetone solution, and photochemical decomposition.

1.4.3 N-nitrosodiphenylamine decomposes in the gas chromatograph inlet forming diphenylamine and, consequently, may be detected as diphenylamine.

2.0 SUMMARY OF METHOD

2.1 Water

A one liter aliquot of sample is acidified to pH 2.0 and extracted with methylene chloride using a continuous liquid-liquid extractor. Separatory funnel extraction is NOT permitted. The methylene chloride extract is dried with sodium sulfate, concentrated, subjected to GPC (GPC is required when higher molecular weight compounds are present that interfere with the analyses of target compounds; GPC is optional for all other circumstances), and analyzed by GC/MS for extractable organics.

2.2 Low Soil/Sediment (Solid Matrices)

A thirty (30) gram portion of soil/sediment/solid is mixed with anhydrous powdered sodium sulfate and extracted with 1:1 methylene chloride/acetone solution using an ultrasonic probe. If the low level screen (Appendix A) is used, a portion of this dilute extract is concentrated fivefold and screened by GC/FID. If peaks are present at greater than 10,000 µg/kg, discard the extract and prepare the sample by the medium level method. If no peaks are present at greater than 10,000 µg/kg the entire extract is concentrated, subjected to GPC cleanup, and analyzed by GC/MS for extractable organics.

2.3 Medium Soil/Sediment (Solid Matrices)

Approximately one gram portion of soil/sediment/solid is mixed with anhydrous powdered sodium sulfate in a vial and extracted with methylene chloride using an ultrasonic probe. The methylene chloride extract can be screened for extractable organics by GC/FID or GC/MS. A method for screening by GC/FID is found in Appendix A. If organic compounds are detected by the screen, the methylene chloride extract is subjected to GPC cleanup and analyzed by GC/MS for extractable organics. If no organic compounds are detected by the medium level screen, then a low level sample preparation is required.

2.4 Oily Sludges (Waste)

A one gram portion of a methylene chloride soluble sample is quantitatively diluted with methylene chloride. The methylene chloride solution can be screened for extractable organics by GC/FID or GC/MS to determine appropriate GC/MS dilution factors. A method for screening by GC/FID is found in Appendix A. The methylene chloride solution is subjected to GPC cleanup and analyzed by GC/MS for extractable organics.

2.5 Method Detection Limits

Prior to analysis, method detection limits (MDLs) for all compounds in Exhibit C, SVOA TCL, must be established in accordance with 40 Code of Federal Regulations, Part 136, Appendix B. The MDL study must be reported as detailed in Exhibit B. All MDL values must be less than or equal to one-third of the CRQL. The MDL study must be conducted using the same specifications as for sample analysis. These specifications include but are not limited to: extraction method, tune conditions and technical acceptance criteria, method blank conditions and technical acceptance criteria, initial and continuing calibration conditions and technical acceptance criteria and all instrument operating conditions. The MDL study must be conducted prior to sample analysis, for each alternate column/technique and/or at least annually, whichever, is more frequent. Seven aliquots of reagent water and/or appropriate clean matrix (such as muffled sand) spiked at 3-5 times the expected MDL are analyzed. Separate MDL studies must be conducted for continuous liquid-liquid extraction and low level soil/sediment/solid sonication methods. An MDL study is not required for waste dilutions. All sequential analyses of MDL standards must be reported and used in the resulting MDL values which are calculated. The MDL results are calculated as described in 40 CFR, Part 136, Appendix B and reported as a separate SDG in accordance with Exhibit B. The appropriate Students' t value must be clearly provided with the algorithm used to calculate the MDL values. MDLs shall be determined and reported for each instrument/column and method.

The MDL study must be reported as detailed in Exhibit B. The individual analytical sequence raw data must be provided and these data must be

summarized in a table which demonstrates the calculated MDL values. The summarized MDL results table must include the concentration found for each compound in each aliquot, the mean concentration of each compound, the percent recovery of each compound, the standard deviation for each compound, and the Method Detection Limit. The true concentration of the compound in the spike solution must also be provided. The table must list the compounds in the same order as they appear in the target compound list in Exhibit C. In addition, the MDL values for each instrument and method used in reporting results for an SDG shall be submitted with each data package.

The annually determined MDL for an instrument and method shall always be used as the MDL for that instrument/method during that year. If the instrument/method is adjusted in any way that may affect the MDL, the MDL for that instrument/method must be redetermined and the results submitted for use as the established MDL for that instrument/method for the remainder of the year.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

Contaminants in solvents, reagents, glassware, and other sample processing hardware may cause method interferences such as discrete artifacts and/or elevated baselines in the extracted ion current profiles (EICPs). All of these materials routinely must be demonstrated to be free from interferences under the extraction and analysis conditions of the method by running laboratory method blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

5.0 SAFETY

The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS) should be made available to all personnel involved in these analyses. Specifically, concentrated sulfuric acid presents some hazards and is moderately toxic and extremely irritating to skin and mucous membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with these reagents.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, catalog and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of this Statement of Work is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the SDG Narrative.

6.1 Glassware

6.1.1 Continuous Liquid-Liquid Extractors - equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf extractor, Ace Glass Company, Vineland, NJ P/N 6841-10 or equivalent) or Hydrophobic Membrane-based Extractor (Accelerated One Step™ Extractor, Corning series 3195 or equivalent).

6.1.2 Beakers - 400 mL.

6.1.3 Syringes - 2 µL, 10 µL, 0.2 mL, 0.5 mL and 10 mL with Luerlok fitting.

6.1.4 Glass Scintillation Vials - at least 20 mL, with screw-cap and Teflon or aluminum foil liner.

6.1.5 Pasteur Pipets - 1 mL glass, disposable.

6.1.6 Vials and Caps - amber glass, 2 mL capacity with Teflon-lined screw cap, 2 mL capacity for GC auto sampler.

6.1.7 Pipets - glass volumetric 1 mL or 2 mL.

6.1.8 Centrifuge Tube - 12 to 15 mL with 19 mm ground glass joint (optional).

6.1.9 Graduated Cylinder - 1 L capacity.

6.1.10 Drying Column - 19 mm ID chromatographic column with coarse frit (substitution of a small pad of Pyrex glass wool for the frit will help prevent cross contamination of sample extracts).

6.2 Kuderna-Danish (K-D) Apparatus

6.2.1 Concentrator Tubes - 15 mL and 10 mL graduated (Kontes K-570050-1025 or K-570040-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground-glass stoppers are used to prevent evaporation of extracts.

6.2.2 Evaporative Flasks - 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

6.2.3 Snyder Column - three-ball macro (Kontes K-503000-0121 or equivalent).

6.2.4 Snyder Column - two-ball micro (Kontes K-569001-0219 or equivalent).

6.3 Spatula - stainless steel or Teflon

6.4 Balances - analytical, capable of accurately weighing ± 0.0001 g, and a top-loading balance capable of weighing 100 g ± 0.01 g. The balances must be calibrated in accordance with ASTM E 617 specifications each 12-hour work shift. The balances must also be annually checked by a certified technician.

6.5 Ultrasonic Cell Disruptors - Heat Systems, Ultrasonics Inc., Model W-385 Sonicator (475 watt with pulsing capability, No.200, ½ inch tapped disruptor horn, No. 419, 1/8 inch standard tapered Microtip probe, and No. 305, 3/4 inch tapped high gain "Q" disruptor horn, or No. 208 3/4 inch standard solid disruptor horn), or equivalent devices with a minimum of 375 watt output capability. NOTE: In order to ensure that sufficient energy is transferred to the sample during extraction, the

Microtip probe or horn shall be replaced if the tip begins to erode. Erosion of the tip is evidenced by a rough surface.

6.6 Sonabox Acoustic Enclosure (or equivalent) - for use with disruptor to decrease noise level.

6.7 Ultrasonic Water Bath

6.8 Vacuum Filtration Apparatus

6.8.1 Buchner Funnel - 9 cm diameter, for filtration.

6.8.2 Filter Paper - Whatman No. 41 or equivalent

6.9 Centrifuge - table top (optional).

6.10 Pyrex Glass Wool - rinsed with methylene chloride

6.11 Test Tube Rack

6.12 Silicon Carbide Boiling Chips - approximately 10/40 mesh. Heat to 400 °C for 30 minutes or soxhlet extract with methylene chloride. Teflon Boiling chips rinsed with methylene chloride prior to use are also acceptable.

6.13 Water Bath - heated, with concentric ring cover, capable of temperature control (±2 °C). The bath should be used in a hood.

6.14 Oven - drying

6.15 Desiccator

6.16 Crucibles - porcelain. Disposable aluminum weighing pans are also acceptable.

6.17 Nitrogen Evaporation Device - equipped with a water bath that can be maintained at 35-40 °C. (N-Evap by Organomation Associates, Inc., South Berlin, MA, or equivalent). To prevent the release of solvent fumes into the laboratory, the nitrogen evaporator device must be used in a hood.

6.18 pH Paper - including narrow range capable of measuring a pH of 2.0.

6.19 pH Meter - with a combination glass electrode, calibrate according to manufacturer's instructions. The pH meter shall be calibrated prior to each use in accordance with the Contractor's Standard Operating Procedures (SOPs).

6.20 Magnetic Stirrer Motor and Magnetic Stirring Bars.

6.21 GPC Cleanup System

6.21.1 Gel Permeation Chromatography System - GPC Autoprep model 1002 A or B, Analytical Biochemical Laboratories, Inc., or equivalent. Systems that perform satisfactorily have been assembled from the following components - an HPLC pump, an auto sampler or a valving system with sample loops, and a fraction collector. All systems, whether automated or manual, must meet the calibration requirements of Section 10.3.3.

6.21.2 NOTE: GPC cleanup is <u>required</u> for all soil/sediment/solid and oily sludge extracts, and for any water extracts containing higher molecular weight contaminants that interfere with the analyses of the target compounds.

6.21.3 Chromatographic Column - 700 mm x 25 mm ID glass column. Flow is upward. To simplify switching from the UV detector during calibration to the GPC collection device during extract cleanup, an optional double 3-way valve (Rheodyne Type 50 Teflon Rotary Valve #10-262 or equivalent) may be attached so that the column exit flow can be shunted either to the UV flow-through cell or to the GPC collection device.

6.21.4 Guard Column (optional) - 5 cm, with appropriate fittings to connect the inlet side of the analytical column (Supelco 5-8319 or equivalent).

6.21.5 Bio Beads (S-X3) - 200-400 mesh, 70 g (Bio-Rad Laboratories, Richmond, CA, Catalog 152-2750 or equivalent). An additional 5 g of Bio Beads are required if the optional guard column is employed. The quality of Bio Beads may vary from lot to lot because of excessive fines in some lots. In addition to fines having a detrimental effect on chromatography, they can also pass through the column screens and damage the valve.

6.21.6 Ultraviolet Detector - fixed wavelength (254 nm) with a semi-prep flow-through cell.

6.21.7 Strip chart recorder, recording integrator or laboratory data system.

6.21.8 Syringe Filter Assembly, disposable - Bio-Rad "Prep Disc" sample filter assembly #343-0005, 25 mm, and 5 micron filter discs or equivalent. Note: Some instrument manufacturer's recommend a smaller micron size filter disc. Consult your instrument operation manual to determine the proper filter disc to use in your system. Check each batch for contaminants by analyzing a GPC blank each time the system is used. Rinse each filter assembly (prior to use) with methylene chloride, if necessary.

6.22 Gas Chromatograph/Mass Spectrometer (GC/MS) System

6.22.1 Gas Chromatograph - The gas chromatograph (GC) system must be capable of temperature programming and must maintain an optimal flow rate throughout the GC temperature program operations. The system must be suitable for splitless injection and have all required accessories including syringes, analytical columns, and gases.

6.22.2 Gas Chromatography Columns

A description of the GC column used for analysis shall be provided in the SDG Narrative.

6.22.2.1 Packed columns must not be used.

6.22.2.2 Capillary columns - The recommended minimum length, ID and stationary phase for capillary columns is: 30 m x 0.25 mm ID (or 0.32 mm) bonded-poly(5% diphenyl/95% dimethylsiloxane). Note that this is a minimum requirement for column length. Longer columns may be used. A film thickness of 1.0 micron is recommended because of its larger capacity, however, a film thickness of 0.25 micron may be used.

6.22.2.2.1 Examples of suitable capillary columns are listed below: DB-5 (J&W Scientific); RTx-5 (Restek); SPB-5 (Supelco); AT-5 (Alltech); HP-5 (Hewlett-Packard); CP-Sil 8CB (Chrompack); 007-2 (Quadrex) and BP-5 (SGE).

6.22.2.2.2 The Contractor may choose to use an alternate capillary column. However, the alternate capillary column selected must meet all the method technical acceptance criteria established in the SOW and Exhibit E.

- The GC column must not introduce contaminants which interfere with identification and quantitation of the compounds listed in Exhibit C (Semivolatiles).
- The GC column must be able to accept concentrations up to the high point standard of each target compound without becoming overloaded.
- The GC column must provide equal or better resolution of the target compounds than the columns listed above.
- The alternate GC column must be used for the entire analysis, including the MDL study, initial and continuing calibration, initial calibration verification and all

blank, QC sample and all sample analyses. If a new alternate GC column is chosen after the initial MDL study has been completed, then the MDL study must be reanalyzed using that alternate column. Analytical results generated using any alternate column must meet all technical acceptance criteria established in the SOW and the CRQLs listed in Exhibit C (Semivolatiles).

6.22.2.2.3 The alternate GC column must be designed to optimize performance. Follow manufacturer's instructions for the use of its product. Before use of any column, other than the ones specified in 6.22.2.2.1, the Contractor must meet the criteria listed in 6.22.2.2.2. Once this has been demonstrated, the Contractor must document the column used (brand name, length, diameter, and film thickness) in each SDG Narrative.

6.22.2.2.4 Manufacturer provided technical information concerning the performance characteristics of the GC column must be included in the MDL Study data package to support the use of the alternate column.

6.22.2.3 The carrier gas for routine GC/MS applications is helium. The purge gas can be either helium or nitrogen. High purity gases must be used to ensure a contaminant free GC/MS system. All carrier gas lines must be constructed from stainless steel or copper tubing. Non-polytetrafluoroethylene (PTFE) thread sealants or flow controllers with rubber components are not to be used.

6.22.3 Mass Spectrometer - must be capable of scanning from 35 to 500 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets the tuning acceptance criteria when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet. The instrument must be vented to the outside of the facility or to a trapping system which prevents the release of contaminants in to the instrument room.

6.22.4 GC/MS interface - any gas chromatograph to mass spectrometer interface that produces the data which meets the technical acceptance criteria established in the SOW. Gas chromatograph to mass spectrometer interfaces constructed of all-glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

6.22.5 Data system - a computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media, of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundance versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. Also, for the non-target compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The NIST/EPA/NIH (May 1992 release or most recent release) and/or Wiley (1991 release or most recent release), or equivalent mass spectral library shall be used as the reference library. The most recent release of the reference library must be utilized. The operational data system must be capable of flagging all data files that have been edited manually by laboratory personnel since every manual edit must be flagged on the quantitation reports.

6.22.6 Magnetic tape storage device - must be capable of recording data and suitable for long-term, off-line storage of GC/MS data.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Reagent Water - defined as water in which an interferent is not observed at or above the CRQL for any target or non-target compound. Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g of activated carbon (Calgon Corp., Filtrasorb - 300 or equivalent).

7.1.1.1 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

7.1.1.2 Reagent water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90 °C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

7.1.2 Sodium Thiosulfate - (ACS) granular.

7.1.3 Sulfuric Acid Solution (H_2SO_4) - (1+1) slowly add 50 mL of concentrated H_2S0_4 (sp. gr. 1.84; 18 N) to 50 mL of reagent water.

7.1.4 Acetone, methanol, methylene chloride, iso-octane, 2-propanol, and toluene - pesticide residue analysis grade or equivalent.

7.1.5 Sodium Sulfate - powdered or granular anhydrous reagent grade, heated at 400 °C for four hours in a shallow tray, cooled in a desiccator and stored in a glass bottle (Baker anhydrous powder, catalog #73898; Baker anhydrous granulated, catalog #3375; or equivalent). CAUTION: An open container of sodium sulfate may become contaminated during storage in the laboratory.

7.1.6 Sodium Sulfite - reagent grade.

7.2 Standards

7.2.1 Standards Documentation

The Contractor must provide all standards to be used with this contract. These standards may be used only after they have been certified according to the procedure described in Exhibit E. The Contractor must be able to verify that the standards are certified by producing the manufacturer's certificates and/or generating the documentation as described in Exhibit E. Manufacturer's certificates of analysis must be retained by the Contractor for the term of the contract. The documentation may be requested during an on-site audit.

7.2.2 Stock Standard Solutions

7.2.2.1 Stock standard solutions may be purchased from commercial suppliers or prepared using the following procedure.

7.2.2.1.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure reference material. Dissolve the material in methylene chloride or another suitable solvent and dilute to volume in a 10 mL volumetric flask. Larger weights/volumes may be used at the convenience of the analyst.

7.2.2.1.2 When compound purity is assayed to be 97.0 percent or greater, the weight may be used without correction to calculate the concentration of the stock solution. If the compound purity is assayed to be less than 97.0 percent, the weight must be corrected when calculating the concentration of the stock solution. See Exhibit E (Analytical Standards Requirements).

7.2.2.1.3 Fresh stock standards must be replaced once every twelve months after the preparation date (or the date opened for purchased standards). The standards must be replaced sooner if the standards have degraded or concentrated. Stock standards must be checked for signs of degradation or concentration just prior

to preparing secondary dilution and working standards from them.

7.2.3 Secondary Dilution Standards

7.2.3.1 Using stock standards, prepare secondary dilution standards in methylene chloride that contain the compounds of interest either singly or mixed together. Secondary dilution standard solutions should be prepared at concentrations that can easily be diluted to prepare working standards.

7.2.3.2 Fresh secondary dilution standards must be prepared once every six months after the preparation date (or the date opened for purchased standards). The standards must be replaced sooner if the standard has demonstrated signs of degradation or evaporation.

7.2.4 Working Standards

7.2.4.1 Surrogate Standard Spiking Solution

7.2.4.1.1 The surrogate standard spiking solution contains the following:

Base Neutrals	Acids
Nitrobenzenene-d5	Phenol-d5
Terphenyl-d14	2,4,6-Tribromophenol
2-Fluorobiphenyl	2-Fluorophenol
1,2-Dichlorobenzene-d4	2-Chlorophenol-d4

7.2.4.1.2 Prepare a surrogate standard spiking solution that contains each of the base/neutral compounds at concentrations of 100 µg/mL in methanol and each of the acid compounds at concentrations of 150 µg/mL in methanol. Surrogate standards are added to all samples, blanks, QC samples and calibration solutions. Additional surrogates may be added at the laboratory's discretion. Prepare fresh surrogate spiking solution monthly, or sooner if the solution has degraded or evaporated.

7.2.4.1.3 For oily sludge (waste) samples extracted using the waste dilution technique described in section 10.1.4.6, prepare a surrogate spiking solution containing all of the above compounds at five (5) times the concentrations specified in Section 7.2.4.1.1 above in methylene chloride. Prepare fresh surrogate spiking solution monthly, or sooner if the solution has degraded or evaporated.

7.2.4.2 Matrix Spiking Solution

7.2.4.2.1 The matrix spiking solution consists of the following:

Bases/Neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-methylphenol
N-Nitroso-di-n-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

7.2.4.2.2 Prepare a matrix spiking solution that contains each of the base/neutral compounds above at 100 µg/mL in methanol and the acid compounds at 150 µg/mL in methanol. Matrix spike/matrix spike duplicate samples are prepared and analyzed as described in Section 12.2. Prepare fresh matrix spiking solution monthly, or sooner if the solution has degraded or evaporated.

7.2.4.2.3 For oily sludge (waste) samples extracted using the waste dilution technique described in section 10.1.4.6, the matrix spiking solution shall be made up in methylene chloride at five (5) times the concentration specified above. Prepare fresh matrix spiking solution monthly, or sooner if the solution has degraded or evaporated.

7.2.4.3 GPC Calibration Solution

7.2.4.3.1 Prepare a GPC calibration solution in methylene chloride containing the following analytes at the minimum concentrations listed (in elution order):

Compound	Concentration (mg/mL)
Corn oil	25.0
bis(2-ethylhexyl)phthalate	0.5
Methoxychlor	0.1
Perylene	0.02
Sulfur	0.08

7.2.4.3.2 NOTE: Sulfur is not very soluble in methylene chloride, but it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it, and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds.

7.2.4.3.3 Prepare fresh GPC Calibration Solution monthly, or sooner if the solution has degraded or evaporated.

7.2.4.4 GC/MS Instrument Performance Check Solution

Prepare a solution of decafluorotriphenylphosphine (DFTPP), such that a 2 µL injection will contain 50 ng of DFTPP. The DFTPP may also be included in the calibration standards at this level. Prepare fresh GC/MS Instrument Performance Check Solution weekly, or sooner if the solution has degraded or evaporated.

7.2.4.5 Internal Standard Solution

7.2.4.5.1 An internal standard solution can be prepared by dissolving 100 mg of each of the following compounds in 50 mL of methylene chloride: 1,4-dichlorobenzene-d4, naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12. It may be necessary to use 5.0 to 10.0 percent toluene in this solution and a few minutes of ultrasonic mixing in order to dissolve all the constituents. The resulting solution will contain each standard at a concentration of 2000 ng/µL. Commercially prepared internal standard solutions are available at suitable concentrations and may be used. All standards must meet the Analytical Standards Requirements of Exhibit E.

7.2.4.5.2 A 10 µL portion of the internal standard spiking solution should be added to each 1.0 mL of sample, standard, blank or QC sample extract just prior to analysis by GC/MS. This will result in 40 ng of each internal standard in the 2 µL volume of extract injected into the GC/MS. Prepare fresh Internal Standard Spiking Solution weekly, or sooner if the solution has degraded or evaporated.

Note: For automated systems using an injection volume of less than 10 μL, the internal standard solution may need to be prepared at a different concentration. Prepare the internal standard solution such that the aliquot used by the system maintains the required 40 ng of each internal standard in the 2 μL volume of extract injected into the GC/MS.

7.2.4.6 Initial and Continuing Calibration Standard Solutions

7.2.4.6.1 Initial Calibration Solutions - Prepare calibration standards at a minimum of five concentration levels (20, 50, 80, 120, and 160 total ng per 2 µL) in methylene chloride. Each calibration standard should contain all of the semivolatile target compounds and surrogate compounds. Eight compounds (2,4-Dinitrophenol, 2,4,5-Trichlorophenol, 2-Nitroaniline, 3-Nitroaniline, 4-Nitroaniline, 4-Nitrophenol, 4,6-Dinitro-2-methylphenol, and Pentachlorophenol) will require only a four-point initial calibration at 50, 80, 120, and 160 total ng per 2 µL, since detection at less than 50 ng per injection is difficult. Initial calibration standard solutions must be prepared fresh each time an initial calibration is analyzed.

7.2.4.6.2 In order to facilitate the confirmation of single component pesticides from the semivolatile library search data (see Exhibit D-Pesticides/Aroclors), the laboratory may include the single component pesticide target compounds listed in Exhibit C in the semivolatile continuing calibration standard. The laboratory may add any or all of these compounds to the semivolatile continuing calibration standard, but at a concentration of 10 ng/µL or less. Do not include the Aroclors or toxaphene mixtures in the semivolatile initial and continuing calibration standards. If the target pesticide compounds are added to this GC/MS standard, these additional analytes are not reported on the semivolatile calibration form (Form VII), but must be included in the quantitation report for the continuing calibration standard. As only a single point calibration would be performed, no %RSD or percent difference criteria would apply to these additional analytes.

7.2.4.6.3 Continuing Calibration Solution - The 50 ng/2 µL calibration standard is the continuing calibration standard. Prepare a fresh Continuing Calibration Solution weekly, or sooner if the solution has degraded or evaporated.

7.2.4.7 Initial Calibration Verification Standard Solution

Prepare an initial calibration verification standard solution of all the semivolatile target compounds in methylene chloride at the same concentration specified for the Continuing Calibration Standard Solution described in Section 7.2.4.6.3. The standard must be from source/supplier other than the source of the initial

calibration standards. Prepare a fresh initial calibration verification standard solution each time an initial calibration is analyzed.

7.2.5 Ampulated Standard Extracts

Standard solutions purchased from a chemical supply house as ampulated extracts in glass vials may be retained for 2 years from the manufacturer's preparation date, unless the manufacturer recommends a shorter time period. Standard solutions prepared by the Contractor which are immediately ampulated in glass vials may be retained for 2 years from the preparation date. Upon breaking the glass seal, the expiration times listed in applicable standard preparation sections will apply. The Contractor is responsible for assuring that the integrity of the standards have not degraded by following proper storage procedures (see Section 7.3).

7.3 Storage of Standard Solutions

7.3.1 Store the stock and secondary dilution standard solutions at 4 °C (± 2 °C) in Teflon-lined screw-cap amber bottles. Fresh stock standards should be replaced or prepared every twelve months at a minimum.

7.3.2 Store the working standards at 4 °C (± 2 °C) in Teflon-sealed containers and protect from light. The standard solutions must be checked frequently for stability. Replace all working standard solutions after six months, or sooner if comparison with quality control check samples indicates a problem. CAUTION: Analysts must allow all standard solutions to equilibrate to room temperature before use.

7.3.3 The continuing calibration standard (50 ng/2 µl) should be prepared weekly and stored at 4 °C (± 2 °C). Refrigeration of the GPC calibration solution may cause the corn oil to precipitate. Before use, allow the solution to stand at room temperature until the corn oil dissolves.

7.3.4 Protect all standards from light. Samples, sample extracts and standards must be stored separately.

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Sample Collection and Preservation

8.1.1 Water samples may be collected in 1 L amber glass containers, fitted with screw-caps lined with Teflon. If amber containers are not available, the samples should be protected from light. Soil samples may be collected in glass containers or closed end tubes (e.g., brass sleeves) in sufficient quantity to perform the analysis. The specific requirements for site sample collection are outlined by the Region.

8.1.2 If samples are received in containers other than glass, then the Contractor shall contact the RSCC to ascertain the proper procedure for subsampling from the sample container.

8.1.3 All samples must be iced and/or refrigerated at 4 °C (±2 °C) from the time of collection until extraction.

8.2 Procedure for Sample Storage

8.2.1 The samples must be protected from light and refrigerated at 4 °C (±2 °C) from the time of receipt until 60 days after delivery of a complete, reconciled data package to the Agency. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 If sample storage temperatures exceed 4°C (±2 °C) and/or samples are not light protected, then the Contractor shall contact the RSCC to ascertain whether or not the samples should be analyzed. For all samples that were not properly refrigerated and/or light protected, the Contractor shall note the problem, the EPA sample numbers for the affected samples, and the Regional instructions in the SDG Narrative.

8.2.3 The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.3 Procedure for Sample Extract Storage

8.3.1 Sample extracts must be protected from light and stored at 4 °C (± 2 °C) until 365 days after delivery of a reconciled, complete data package to the Agency.

8.3.2 Samples, sample extracts, and standards must be stored separately.

8.4 Contract Required Holding Times

8.4.1 Extraction of water samples by continuous liquid-liquid procedures shall be started within 5 days of Validated Time of Sample Receipt (VTSR). Extraction of soil/sediment/solid samples by sonication procedures shall be completed within 10 days of VTSR. Oily sludge waste dilutions shall be completed within 10 days of VTSR. Note: Separatory funnel extraction procedures are not permitted.

8.4.2 As part of the Agency's QA program, the Agency may provide Performance Evaluation samples which the Contractor is required to prepare per the instructions provided by the Agency. The extraction holding time (5 days after VTSR for water and 10 days after VTSR for soil/sediment) does not apply to Performance Evaluation samples. The PE samples must be analyzed and reported with the SDG with which they were submitted.

8.4.3 Extracts of water, soil/sediment/solid samples and oily sludge (waste) samples must be analyzed within 40 days of the start of extraction.

8.4.4 If semivolatile samples have exceeded contract required holding times and have not yet been analyzed, then the Contractor shall contact the RSCC to ascertain whether or not the samples should be analyzed. Note that this notification requirement in no way obviates the contractual requirement for the Contractor to analyze samples within holding times. If the Contractor is instructed to proceed with analysis outside holding times, sample price may be reduced depending upon the impact of the non-compliance on data usability. For all samples that exceeded holding times, the Contractor shall note the

problem, the EPA sample numbers for the affected samples, and the Regional instructions in the SDG narrative.

8.4.5 Semivolatile data reported from sample preparation and/or analyses which were performed outside the contract required holding times for extraction and/or analysis shall be subject to a commensurate reduction in sample price or zero payment due to data rejection depending upon the impact of the non-compliance on data usability.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Conditions

9.1.1 Gas Chromatograph

9.1.1.1 The following are the gas chromatographic analytical conditions. The conditions are recommended unless otherwise noted.

Initial Column Temperature Hold	40 °C for 4 minutes
Column Temperature Program	40-270 °C at 10 C°/min.
Final Column Temperature Hold	270 °C; Hold Required for 3 minutes after all TCL in Exhibit C (SVOA) have eluted
Injector Temperature	250-300 °C
Transfer Line Temperature	250-300 °C
Source Temperature	According to manufacturer's specifications
Injector	Grob-type, splitless
Sample Volume	2 µL
Carrier Gas	Helium at 30 cm/sec

9.1.1.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, samples, blanks and QC samples.

9.1.2 Mass Spectrometer

The following are the required mass spectrometer analytical conditions:

Electron Energy	70 volts (nominal)
Mass Range	35 to 500 amu
Scan Time	Not to exceed 1 second per scan

9.2 GC/MS Instrument Performance Check (Tuning) and Ion Abundance

9.2.1 Summary of GC/MS Instrument Performance Check

9.2.1.1 The Mass Spectrometer must be tuned to meet the manufacturer's specifications, using a suitable calibrant such as perfluoro-tri-N-butylamine (PFTBA) or perfluorokerosene (PFK).

9.2.1.2 The mass calibration and resolution of the GC/MS system are verified by the analysis of the instrument performance check solution (DFTPP -Section 7.2.4.4). Prior to the analysis of any samples; including QC samples, blanks or calibration standards, the Contractor must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check solution containing decafluorotriphenylphosphine (DFTPP).

9.2.1.3 If the technical acceptance criteria for GC/MS Instrument Performance Check are not met, then the contractor must stop and correct the problem before continuing the analytical sequence.

9.2.2 Frequency of GC/MS Instrument Performance Check

9.2.2.1 The GC/MS instrument performance check solution must be analyzed once at the beginning of each 12-hour period during which standards, samples, QC samples or blanks are analyzed.

9.2.2.2 The 12-hour time period for a GC/MS instrument performance check, standards calibration (initial or continuing calibration criteria), blank, QC sample and sample analysis begins at the moment of injection of the DFTPP analysis that the laboratory submits as documentation of a compliant instrument performance check. The time period ends after 12 hours have elapsed according to the system clock.

9.2.3 Procedure for GC/MS Instrument Performance Check

The analysis of the GC/MS instrument performance check solution may be performed as an injection of up to 50 ng of DFTPP into the GC/MS or by adding 50 ng of DFTPP to the calibration standards (Section 7.2.4.5) and analyzing the calibration standard. DFTPP key ion abundances are compared to established ion abundance criteria for DFTPP outlined in Table 1.

9.2.4 Technical Acceptance Criteria for GC/MS Instrument Performance Check

9.2.4.1 The GC/MS system must be tuned at the frequency described in Section 9.2.2.

9.2.4.2 The mass spectrum of DFTPP must be acquired in the following manner: Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. Do not subtract part of the DFTPP peak. The abundance criteria listed in Table 1 must be met for a 50 ng injection of DFTPP.

9.2.4.3 All subsequent standards, samples, QC samples and blanks associated with a DFTPP analysis must use the identical mass spectrometer instrument conditions.

9.2.5 Corrective Action for GC/MS Instrument Performance Check

9.2.5.1 If the DFTPP technical acceptance criteria are not met, re-tune the GC/MS system. If the GC/MS system cannot be retuned, then it may be necessary to clean the ion source or take other actions to achieve the technical acceptance criteria.

9.2.5.2 DFTPP acceptance criteria MUST be met before any standards, samples, including QC samples or required blanks are analyzed. Any standards, samples, QC samples or required blanks analyzed when GC/MS Instrument Performance Check technical acceptance criteria have not been met will require reanalysis at no additional cost to the Agency. Reanalyses must be performed within contract required holding times and must meet all technical acceptance criteria.

9.2.5.3 Sample analyses reported with a non-compliant GC/MS Instrument Performance Check after reanalysis shall receive a commensurate reduction in sample price or zero payment due to data rejection depending upon the impact of the non-compliance on data usability.

9.3 Initial Calibration

9.3.1 Summary of Initial Calibration

9.3.1.1 Prior to the analysis of samples, QC samples and required blanks, and after the GC/MS instrument performance check technical acceptance criteria have been met, each GC/MS system must be calibrated at a minimum of five concentrations (Section 7.2.4.6) to determine instrument sensitivity and the linearity of GC/MS response for the semivolatile target and surrogate compounds.

9.3.1.2 If the technical acceptance criteria for initial calibration are not met, then the Contractor must stop and correct the problem before continuing the analytical sequence.

9.3.2 Frequency of Initial Calibration

9.3.2.1 Each GC/MS system must be initially calibrated upon award of the contract, whenever the contractor takes corrective action which may change or affect the initial calibration criteria (e.g., ion source cleaning or repairs, column replacement, etc.), or if the continuing calibration technical acceptance criteria have not been met.

9.3.2.2 If time still remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration, samples

may be analyzed. It is not necessary to analyze a continuing calibration standard within this 12-hour time period, if the initial calibration standard that is the same concentration as the continuing calibration standard meets the continuing calibration technical acceptance criteria. Quantify all sample and QC sample results and evaluate quality control criteria results, such as internal standard area response change and retention time shift, against the initial calibration standard that is the same concentration as the continuing calibration standard (50 ng/2 µL).

9.3.3 Procedure for Initial Calibration

9.3.3.1 All standard/spiking solutions and blanks must be allowed to warm to ambient temperature (approximately 1 hour) before preparation or analysis.

9.3.3.2 Prepare five calibration standards containing all the semivolatile target and surrogate compounds at the concentrations described in Section 7.2.4.6.

9.3.3.3 Add a 10 µL aliquot of internal standard solution (Section 7.2.4.5.2) to each 1.0 mL aliquot of calibration standards to result in 40 ng of internal standard in the 2 µL volume of calibration standard injected onto the GC/MS. The internal standards specified in Section 7.2.4.5.1 should permit most of the semivolatile target compounds to have relative retention times of 0.80 to 1.20, using the assignments of internal standards to target compounds given in Table 2.

9.3.3.4 Analyze each calibration standard by injecting 2.0 µL of standard.

9.3.4 Calculations for Initial Calibration

9.3.4.1 Calculate the relative response factor (RRF) for each semivolatile target and surrogate compound using Equation 1. The primary characteristic ions used for quantitation of target compounds, surrogate compounds and internal standards are listed in Table 3 and Table 4. Assign each target compound, and surrogate compound to an internal standard according to Table 2. If an interference prevents the use of a primary ion for a given target compound or internal standard, use a secondary ion listed in Table 3 or 4. NOTE: Unless otherwise stated, the area response of the primary characteristic ion must be the quantitation ion. If a secondary ion is used for quantitation in a sample, the initial and continuing calibration standards must also be calculated using the secondary ion.

EQ. 1

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where,

A_x = Area of the characteristic ion for the compound to be measured (see table 4)
A_{is} = Area of the characteristic ion for specific internal standard (see table 3)
C_{is} = Amount of the internal standard injected (ng)
C_x = Amount of the compound to be measured injected (ng)

9.3.4.2 The mean relative response factor (RRF) must be calculated for all compounds using the following equation:.

EQ. 2

$$\overline{RRF} = \frac{\sum_{i=1}^{n} RRF_i}{n}$$

Where,

$\overline{RRF}$ = Mean Relative Response Factor.
RRF_i = Individual RFs used to calculate the mean.
n = The total number of values.

9.3.4.3 Calculate the % Relative Standard Deviation (%RSD) of the RRF values for the initial calibration using the following equation:

EQ. 3

$$\%RSD = \frac{Standard\ Deviation}{\overline{RRF}} \times 100$$

Where,

$$Standard\ Deviation_{RRF} = \sqrt{\frac{\sum_{i=1}^{n} (RRF_i - \overline{RRF})^2}{(n-1)}}$$

$\overline{RRF}$, RRF_i and n are defined above.

9.3.5 Technical Acceptance Criteria for Initial Calibration

9.3.5.1 All initial calibration standards must be analyzed at the concentration levels described in Section 7.2.4.6 and at the frequency described in Section 9.3.2 on a GC/MS system meeting the GC/MS Instrument Performance Check (DFTPP) technical acceptance criteria.

9.3.5.2 The relative response factor (RRF) at each calibration concentration for each semivolatile target and surrogate compound must be greater than or equal to the compound's minimum acceptable relative response factor listed in Table 5.

9.3.5.3 The %RSD over the initial calibration range for the relative response factors for each semivolatile and surrogate compound must be less than or equal to the maximum %RSD listed in Table 5.

9.3.5.4 Up to four compounds may fall outside the criteria listed in Table 5. However, these four compounds must meet a minimum RRF criterion of 0.010 and have a %RSD less than or equal to 40.0 percent.

9.3.5.5 Excluding those ions in the solvent front, quantitation ions for any target compound may not saturate the detector, with the exception of quantitation ions in up to 3 compounds (including internal standards and surrogates) from the high standard (160 ng/2 µL). Consult the manufacturer's instrument manual to determine how saturation is indicated for your instrument.

9.3.6 Corrective Action for Initial Calibration

9.3.6.1 If the initial calibration technical acceptance criteria are not met, inspect the entire analytical system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to achieve the technical acceptance criteria.

9.3.6.2 Initial calibration technical acceptance criteria **must** be met before any samples, including QC samples or required blanks are analyzed. Any samples, including QC samples or required blanks analyzed when initial calibration technical acceptance criteria have not been met will require reanalysis at no additional cost to the Agency. Reanalyses must be performed within contract required holding times and must meet all sample technical acceptance criteria.

9.3.6.3 Sample analyses reported with a non-compliant initial calibration after reanalysis shall receive a commensurate reduction in sample price or zero payment due to data rejection depending upon the impact of the non-compliance on data usability.

9.4 Initial Calibration Verification

9.4.1 Summary of Initial Calibration Verification

9.4.1.1 Prior to the analysis of samples, QC samples, required blanks and after the GC/MS instrument performance check solution criteria and initial calibration technical acceptance criteria have been met, the initial calibration must be verified using a separate source standard.

9.4.1.2 If the technical acceptance criteria for the initial calibration verification are not met, then the Contractor must stop and correct the problem before continuing the analytical sequence.

9.4.2 Frequency of Initial Calibration Verification

9.4.2.1 A second source verification of the initial calibration standards must be performed by the Contractor upon award of the contract, whenever an initial calibration is performed and whenever the Contractor takes corrective action which may change or affect the initial calibration technical acceptance criteria (e.g., ion source cleaning or repair, column replacement, etc.).

9.4.3 Procedure for Initial Calibration Verification

9.4.3.1 All standard/spiking solutions and blanks must be allowed to warm to ambient temperature (approximately 1 hour) before preparation or analysis.

9.4.3.2 Add a 10 µL aliquot of internal standard solution (Section 7.2.4.5.2) to a 1 mL aliquot of the initial calibration verification standard solution (Section 7.2.4.7) to result in 40 ng of internal standard in the 2 µL volume injected onto the GC/MS.

9.4.4 Calculations for Initial Calibration Verification

9.4.4.1 Calculate the relative response factor (RRF) for each semivolatile target and surrogate compound in the initial calibration verification standard using Equation 1.

9.4.4.2 Calculate the percent difference between the initial calibration verification standard relative response factor and the most recent initial calibration mean relative response factor for each semivolatile target and surrogate compound using Equation 4.

EQ. 4

$$\%Difference = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

Where,

RRF_c = Relative response factor from initial calibration verification standard

$\overline{RRF_i}$ = Mean relative response factor from the most recent initial calibration meeting technical acceptance criteria

Note: The initial calibration verification results must be reported on an appropriate form and must be included in the data package with the associated initial calibration data.

9.4.5 Technical Acceptance Criteria for the Initial Calibration Verification

9.4.5.1 The initial calibration verification standard must be analyzed at the concentration level described in Section 7.2.4.7, and at the frequency described in Section 9.4.2 on a GC/MS system meeting the GC/MS Instrument Performance check and initial calibration technical acceptance criteria.

9.4.5.2 The relative response factor (RRF) for each target semivolatile and surrogate compound must be greater than or equal to the compounds's minimum acceptable response factor listed in Table 5.

9.4.5.3 The relative response factor percent difference (%D) for each target semivolatile and surrogate compound must be less than or equal to $\pm$ 30.0 percent.

9.4.5.4 Up to four compounds may fail the requirements listed in Sections 9.4.5.2 and 9.4.5.3 and still meet the minimum relative response factor criteria and percent difference criteria. However, these compounds must have a minimum relative response factor greater than or equal to 0.010 and the percent difference must be within the inclusive range of $\pm$ 40.0 percent.

9.4.5.5 Excluding those ions in the solvent front, quantitation ions for any target compound may not saturate the detector, with the exception of quantitation ions in up to 3 compounds (including internal standards and surrogates) from the high standard (160 ng/2 µL). Consult the manufacturer's instrument manual to determine how saturation is indicated for your instrument.

9.4.6 Corrective Action for Initial Calibration Verification

9.4.6.1 If the initial calibration verification criteria are not met, reanalyze and check the initial calibration verification solution following Sections 9.4.3 and 9.4.4. If the reanalysis meets the technical acceptance criteria established in Section 9.4.5, then proceed with sample analysis.

9.4.6.2 If the reanalysis still does not meet the technical acceptance criteria, examine the preparation procedures and calculations which were used to make the initial calibration and initial calibration verification solutions. If the procedures or calculations were incorrect, correct the calculations and verify the initial calibration and initial calibration verification technical acceptance criteria. It may be necessary to take other corrective actions to achieve the initial calibration technical acceptance criteria.

9.4.6.3 Initial calibration verification technical acceptance criteria **must** be met before any samples, QC samples, or required blanks are analyzed. Any continuing calibration, samples, QC samples or required blanks analyzed when the initial calibration verification technical acceptance criteria have not been met must be reanalyzed at no additional cost to the Agency. Reanalyses must be performed within contract required holding times and must meet all sample technical acceptance criteria.

9.4.6.4 Sample results reported with a non-compliant initial calibration verification standard shall receive a commensurate reduction in sample price or zero payment due to data rejection depending upon the impact of the non-compliance on data usability.

9.5 Continuing Calibration

9.5.1 Summary of Continuing Calibration

9.5.1.1 Prior to the analysis of samples, including QC samples and required blanks, and after GC/MS instrument performance check, initial calibration and initial calibration verification technical acceptance criteria have been met, each GC/MS system must be routinely checked by analyzing a continuing calibration standard to ensure that the GC/MS instrument continues to meet the instrument sensitivity requirements of the SOW. The continuing calibration standard contains all the semivolatile target and surrogate compounds.

9.5.1.2 If the technical acceptance criteria for continuing calibration are not met, then the Contractor must stop and correct the problem before continuing the analytical sequence.

9.5.2 Frequency of Continuing Calibration

9.5.2.1 Each GC/MS used for analysis must be calibrated once every 12-hour time period of operation. The 12-hour time period begins with the injection of the GC/MS instrument performance check solution (DFTPP).

9.5.2.2 If time still remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration, samples may be analyzed. It is not necessary to analyze a continuing

calibration standard within this 12-hour time period, if the initial calibration standard that is the same concentration as the continuing calibration standard meets the continuing calibration technical acceptance criteria. Quantitate all sample results against the initial calibration standard that is the same concentration as the continuing calibration standard (50 ng/2 µL).

9.5.2.3 If time does **not** remain in the 12-hour time period, a new analysis of the GC/MS instrument performance check solution must be made. If the reanalysis meets the ion abundance criteria for DFTPP, then a continuing calibration standard may be analyzed.

9.5.3 Procedure for Continuing Calibration

9.5.3.1 All standard/spiking solutions and blanks must be allowed to warm to ambient temperature (approximately 1 hour) before preparation or analysis.

9.5.3.2 Add a 10 µL aliquot of internal standard solution (Section 7.2.4.5.2) to a 1 mL aliquot of the continuing calibration standard solution to result in 40 ng of internal standard in the 2 µL volume injected onto the GC/MS.

9.5.3.3 Analyze the continuing calibration standard by injecting 2.0 µL of standard.

9.5.4 Calculations for Continuing Calibration

9.5.4.1 Calculate a relative response factor (RRF) for each semivolatile target and surrogate compound using Equation 1 and the primary characteristic ions found in Table 3 (Internal Standards) and Table 4 (Target Compounds and Surrogates). For internal standards, use the primary ions listed in Table 3 unless interferences are present. If interferences prevent the use of the primary ion for a given internal standard, use the secondary ion(s) listed in Table 3.

9.5.4.2 Calculate the percent difference (%D) between the mean relative response factor from the most recent initial calibration and the continuing calibration relative response factor for each semivolatile target and surrogate compound using Equation 4.

9.5.5 Technical Acceptance Criteria for Continuing Calibration

9.5.5.1 The continuing calibration standard must be analyzed at the 50 ng/2 µL concentration level at the frequency described in Section 9.5.2, on a GC/MS system meeting the GC/MS Instrument performance check (DFTPP), initial calibration and initial calibration verification technical acceptance criteria.

9.5.5.2 The relative response factor (RRF) for each semivolatile target and surrogate compound must be greater than or equal to the compound's minimum acceptable RRF listed in Table 5.

9.5.5.3 The relative response factor percent difference (%D) for each semivolatile target and surrogate compound must be less than or equal to the value listed in Table 5.

9.5.5.4 Up to four semivolatile target compounds may fall outside the minimum RRF or maximum % D criteria listed in Table 5, but the RRFs of those four compounds must be greater than or equal to 0.010, and the percent differences must be within the inclusive range of ± 40.0 percent.

9.5.5.5 Excluding those ions in the solvent front, quantitation ions for any target compound may not saturate the detector. Consult the manufacturer's instrument operating manual to determine how saturation is indicated for your instrument.

9.5.6 Corrective Action for Continuing Calibration

9.5.6.1 If any continuing calibration technical acceptance criteria are not met, recalibrate the GC/MS instrument according to Section 9.3.3. It may be necessary to clean the ion source, change the

column or take other corrective actions to achieve the continuing calibration technical acceptance criteria.

9.5.6.2 Continuing calibration technical acceptance criteria MUST be met before any samples, including QC samples or required blanks are analyzed. Any samples, including QC samples or required blanks analyzed when continuing calibration criteria have not been met will require reanalysis at no additional cost to the Agency. Reanalyses must be performed within contract required holding times and must meet all sample technical acceptance criteria.

9.5.6.3 Sample analyses reported with a non-compliant continuing calibration after reananlysis shall receive a commensurate reduction in sample price or zero payment due to data rejection depending upon the impact of the non-compliance on data usability.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 If insufficient sample amount (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact the RSCC to apprise them of the problem. The Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis. All changes in the analyses **must** be preapproved by the Region I Project Officer. The Contractor shall document the Regional instructions (including sample weight/volume prepared and analyzed) in the SDG Narrative.

10.1.2 If multiphase samples (e.g., a two-phase liquid sample, oily sludge/sandy soil sample) are received by the Contractor, the Contractor shall contact the RSCC to apprise them of the type of sample received. If all phases of the sample are amenable to analysis, the Region may require the Contractor to do one of the following:

- Mix the sample and analyze an aliquot from the homogenized sample.
- Separate the phases of the sample and analyze each phase separately. The RSCC will provide EPA sample numbers for the additional phases, if necessary.
- Separate the phases of the sample and analyze one or more of the phases but not all of the phases. The RSCC will provide EPA sample numbers for the additional phases, if necessary.
- Do not analyze the sample.

10.1.2.1 If all of the phases are not amenable to analysis (i.e., outside scope), then the Region may require the Contractor to do one of the following:

- Separate the phases and analyze the phase(s) that are amenable to analysis. The RSCC will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.2 No other change in the analyses will be permitted. The Contractor shall document the problem, the EPA sample numbers for the affected samples and the Regional instructions in the SDG Narrative.

10.1.3 Water Samples

10.1.3.1 Continuous liquid-liquid extraction is used to extract aqueous samples. Separatory funnel extraction <u>cannot</u> be used.

10.1.3.2 Continuous Liquid-Liquid Extraction Without Hydrophobic Membrane

10.1.3.2.1 Follow manufacturer's instructions for set-up.

10.1.3.2.2 Add methylene chloride to the bottom of the extractor and fill it to a depth of at least one inch above the bottom sidearm.

10.1.3.2.3 Measure out a 1 L sample aliquot in a separate, clean graduated cylinder; transfer the aliquot to the continuous extractor. Adjust the pH to 2.0 with 1:1 H_2SO_4 and verify it with a pH meter or narrow range pH paper. Record the pH and exact volume used of each sample on the sample extraction log. NOTE: With some samples, it may be necessary to place a layer of glass wool between the methylene chloride and the water layer in the extractor to prevent precipitation of suspended solids into the methylene chloride during extraction.

10.1.3.2.4 Using a syringe or volumetric pipet, add 0.5 mL of the surrogate standard spiking solution (7.2.4.1.2) into the sample and mix well.

10.1.3.2.5 Rinse the graduated cylinder with 50 mL of methylene chloride and transfer the rinsate to the continuous extractor. Rinse the empty 1 L sample container with 50 mL of methylene chloride and add the rinsate to the continuous extractor.

10.1.3.2.6 Add sufficient methylene chloride to the continuous extractor to ensure proper solvent cycling during operation. Adjust the drip rate to 5 to 15 mL/minute (recommended); optimize the extraction drip rate. Extract for a minimum of 18 hours. NOTE: When a minimum drip rate of 10-15 mLs/min is maintained throughout the extraction, the extraction time may be reduced to a minimum of 12 hours. Allow to cool, then detach the distillation flask. Proceed to Section 10.2 for extract concentration.

10.1.3.2.7 NOTE: Some continuous liquid-liquid extractors are also capable of concentrating the extract within the extraction set-up. Follow the manufacturer's instructions for concentration when using this type of extractor.

10.1.3.3 Continuous Liquid-Liquid Extraction With Hydrophobic Membrane

10.1.3.3.1 Follow the manufacturer's instructions for set-up.

10.1.3.3.2 Measure out each 1 L sample aliquot in a separate, clean graduated cylinder and transfer the aliquot to the continuous extractor. Adjust the pH to 2.0 with 1:1 H_2SO_4 and verify it with a pH meter or narrow range pH paper. Record the pH on the sample extraction log.

10.1.3.3.3 Using a syringe or volumetric pipet, add 0.5 mL of the surrogate standard spiking solution (7.2.4.1.2) into the sample and mix well.

10.1.3.3.4 Rinse the graduated cylinder with 50 mL of methylene chloride and transfer the rinsate to the continuous extractor. Rinse the empty 1 L sample container with 50 mL of methylene chloride and add the rinsate to the continuous extractor.

10.1.3.3.5 Add sufficient methylene chloride to the continuous extractor to ensure proper solvent cycling during operation. Adjust the drip rate to 15 mL/minute (recommended); optimize the extraction drip rate. Extract for a minimum of 6 hours. (NOTE: Due to the smaller volume of solvent used during the extraction process, some sample matrices (e.g., oily samples, samples containing a high concentration of surfactants) may create an emulsion which will consume the solvent volume, preventing the efficient extraction of the sample. When this occurs, add additional solvent to assure efficient extraction of the sample, and extend the extraction time for a minimum of 6 hours. If the sample matrix prevents the free flow of solvent through the membrane, then the non-hydrophobic membrane continuous liquid-liquid type extractor must be used.) Allow to cool, then detach the distillation flask. Proceed to Section 10.2 for concentration of the extract for GPC cleanup and/or GC/MS analysis.

10.1.3.3.6 NOTE: Some continuous liquid-liquid extractors are also capable of concentrating the extract within the extraction set-up. Follow the manufacturer's instructions for concentration when using this type of extractor. Using the hydrophobic membrane type extractor, it may not be necessary to dry the extract with sodium sulfate.

10.1.3.4 The contractors may choose to use alternate continuous liquid-liquid extractor types. However, the alternate extractor must be used for all extractions and must meet all the method technical acceptance criteria established in the SOW. If an alternate extractor type is chosen after the initial MDL study has been completed, then the MDL study must be reanalyzed using that alternate extractor. If using alternate extractors or design types, follow the manufacturer's instructions for set-up and operation.

10.1.4 Soil/Sediment/Solid Samples

The "sample" is defined as the entire contents of the sample container. Do not discard any supernatant liquids. Just prior to removing the sample for extraction, mix the contents of the sample container throughly either by gentle shaking, if liquid is present, or with a narrow metal spatula. Remove and discard any large foreign objects such as sticks, leaves, and rocks in soil samples. For other types of solid materials, break the sample into small soil-like pieces with a metal spatula to increase the surface area.

10.1.4.1 pH Determination

Transfer 50 g of soil/sediment/solid to a 100 mL beaker. Add 50 mL of water and continuously stir for 1 hour on a magnetic stirrer. Determine the pH of the sample with a calibrated pH meter while stirring. Report the pH value on sample preparation logsheets and on the Form I - SV. If the pH of the soil/sediment/solid is greater than 11 or less than 5, document this in the SDG Narrative. Discard the portion of sample used to determine the pH. If limited sample volume is received use a smaller 1:1 ratio of grams of soil/sediment/solid sample to mLs of reagent water for the pH determination. NOTE: The minimum grams to water ratio for pH determination should be 5 g to 5 ml. The Contractor must note any deviations to the method in the SDG Narrative.

10.1.4.2 Percent Moisture

10.1.4.2.1 Prior to sample analysis, determine the sample's percent moisture. Weigh 5-10 g of the soil/sediment/solid sample into a tared crucible and dry overnight or for at least 12 hours in an oven at 105 °C. Allow the sample to cool in a desiccator before reweighing. Calculate the percent moisture using the equation below. Concentrations of individual compounds will be reported relative to the dry weight of soil/sediment/solid.

EQ. 5

$$\%\ Moisture = \frac{grams\ of\ wet\ sample - grams\ of\ dry\ sample}{grams\ of\ wet\ sample} \times 100$$

10.1.4.2.2 If the percent moisture of the sample as determined above is less than 70 percent (< 70 %), proceed with extraction and analysis for low level soil/sediment/solid samples described in Section 10.1.4.4.

10.1.4.2.3 If the percent moisture of the soil/sediment/solid sample is greater than or equal to 70 percent (≥ 70 %); centrifuge and decant the sample to remove the majority of the water or the sample may be pressure filtered. Determine the percent moisture of the remaining centrifuged/filtered soil/sediment/ solid sample following Section 10.1.4.2.1 above. If the percent moisture of the centrifuged/filtered soil/sediment/ solid sample is less than 70 percent (< 70 %), proceed with extraction and analysis of the centrifuged solid sample using the low level soil/sediment/solid sample method described in Section 10.1.4.4.

10.1.4.2.4 If the percent moisture of the centrifuged/filtered soil/ sediment/solid sample is greater than or equal to 70 percent (≥ 70 %), then the Contractor shall contact the RSCC for directions. The Region may require that the Contractor do one of the following:

- Analyze the centrifuged/filtered soil/sediment/solid sample "as is";
- Use an additional aliquot (weight) of centrifuged/filtered soil/sediment/solid sample (≥ 70 % M) weight for extraction and analysis and/or decrease the final extract volume (to no lower than 0.5 ml) to achieve the dry weight CRQLs;
- Use another method of analysis;
- Do not analyze that sample.

10.1.4.2.5 If percent moisture of the centrifuged/filtered soil/sediment/ solid is greater than ≥ 90 percent, then the Contractor must contact the RSCC for directions. The Region may require that the Contractor do one of the following:

- Analyze the soil/sediment/solid sample (≥ 90 % M) "as is";
- Use an additional aliquot (weight) of soil/sediment/solid sample (≥ 90 % M) weight for extraction and analysis and/or decrease the final extract volume (to no lower than 0.5 ml) to achieve the dry weight CRQLs;
- Use another method of analysis;
- Do not analyze that sample.

10.1.4.2.6 If a sufficient sample weight/volume has not been provided by the sampler to perform the additional percent moisture determinations and/or to extract/analyze an increased portion of sample, then the Contractor shall contact the RSCC to ascertain whether or not the sample should be analyzed.

10.1.4.2.7 For all samples that do not meet the greater than or equal to 70 percent moisture (≥ 70 %M) requirement, the Contractor shall note the problem, the EPA sample numbers for the affected samples, the initial and subsequent percent moisture(s), and the steps taken to achieve the dry weight CRQLs including the sample weight/ volume prepared and analyzed, the final extract volume and any Regional instructions in the SDG Narrative.

10.1.4.3 Mandatory Determination of Concentration Level

10.1.4.3.1 The Contractor must determine whether a solid matrix sample should be analyzed by the low or medium level soil/sediment/ solid method. It is the responsibility of the Contractor to analyze the sample at the correct level.

10.1.4.3.2 Three approaches may be taken to determine whether the low level or medium level method should be followed.

- Assume the sample is low level and analyze a 30 g sample.
- Use an in-house laboratory screening procedure. This procedure must be documented and available for review during on-site laboratory evaluation or when requested by the Region.
- Use the GC/FID screening method in Appendix A to determine the appropriate method for analysis.

10.1.4.4 Low Level Soil/Sediment/Solid Samples

10.1.4.4.1 The following steps should be performed rapidly to avoid loss of the more volatile extractables. Weigh approximately 30 g of sample to the nearest 0.1 g into a 400 mL beaker and add 60 g of anhydrous powdered or granulated sodium sulfate. Mix well. Record the exact weight of sample taken on the sample preparation log and the Form I SV. The sample should have a sandy texture at this point. Add 0.5 mL of the surrogate standard spiking solution (Section 7.2.4.1.2) to the sample, then immediately add 100 mL of 1:1 methylene chloride-acetone.

10.1.4.4.2 Place the bottom surface of the tip of the 3/4 inch tapered disruptor horn about ½ inch below the surface of the solvent but above the soil/sediment/solid layer.

10.1.4.4.3 Sonicate for 3 minutes using a 3/4 inch disruptor horn at full power (output control knob at 10) with pulse on and percent duty cycle knob set at 50.0 percent. Do not use a microtip. NOTE: These settings refer to the Model W-385. When using a sonicator other than Model W-385, refer to the instructions provided by the manufacturer for appropriate output settings. Decant and filter extracts through Whatman #41 filter paper using vacuum filtration or centrifuge.

10.1.4.4.4 Repeat the extraction two more times with additional 100 mL portions of 1:1 methylene chloride-acetone. Before each extraction, make certain that the sodium sulfate is free-flowing and not a consolidated mass. As required, break up large lumps with a clean spatula, or, very carefully, with the tip of the unenergized probe. Filter the extract after each sonication and combine all three extracts. On the final sonication, pour the entire sample into the Buchner funnel and rinse with 1:1 methylene chloride-acetone. If samples are not screened, proceed to Section 10.2.

10.1.4.4.5 If the sample extract is to be screened prior to GPC, remove a 1.0 ml aliquot and follow Appendix A for, "Screening of Semivolatile Organic Extracts." If screening is not performed, proceed to extract concentration in Section 10.2.

10.1.4.4.6 After screening, transfer the remainder of the 1 mL back to the total extract. Concentrate the extract according to the procedures outlined in Section 10.2. CAUTION: To minimize sample loss during screening, autosamplers which pre-flush samples through the syringe should not be used.

10.1.4.5 Medium Level Soil/Sediment/Solid Samples

10.1.4.5.1 Transfer approximately 1 g (to the nearest 0.1 g) of sample to a 20 mL vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of sample taken on the sample preparation log and the Form I SV. Cap the

vial before proceeding with the next sample to avoid any cross-contamina

10.1.4.5.2 Add 2.0 g of anhydrous powdered or granulated sodium sulfate to the sample in the 20 mL vial, and mix well. More sodium sulfate may be added to make sure the sample is free-flowing.

10.1.4.5.3 Surrogates are added to all samples, QC samples and blanks. Add 0.5 mL of surrogate spiking solution (Section 7.2.4.1.2) to the sample mixture.

10.1.4.5.4 Immediately add 9.5 mL of methylene chloride to the sample and disrupt the sample with the 1/8 inch tapered Microtip ultrasonic probe for 2 minutes at output control setting 5, in continuous mode (if using a sonicator other than Models W-375 or W-385, contact the instrument manufacturer for appropriate output settings). Before extraction, make certain that the sodium sulfate is free-flowing and not a consolidated mass. As required, break up large lumps with a clean spatula, or, very carefully, with the tip of the unenergized probe. Proceed with GPC cleanup (Section 10.3).

10.1.4.6 Oily Sludges (Waste)

10.1.4.6.1 Transfer approximately 1 g (to the nearest 0.1 g) of sample to a to a 20 mL vial which has been precalibrated to 10 mL. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of sample taken on the sample preparation log and the Form I SV. Cap the vial before proceeding with the next sample to avoid any cross-contamination.

10.1.4.6.2 Add 2.0 g of anhydrous powdered or granulated sodium sulfate to the sample in the vial and mix well. More sodium sulfate may be added to make sure the sample is free-flowing.

10.1.4.6.3 Surrogates are added to all samples, QC samples and blanks. Add 1.0 mL of the more concentrated surrogate spiking solution (Section 7.2.4.1.3) to the sample mixture.

10.1.4.6.4 Immediately dilute to 10.0 mL with methylene chloride.

10.1.4.6.5 Cap tightly and sonicate in a sonicator bath for 2 minutes.

10.1.4.6.6 Proceed with GPC cleanup (Section 10.3).

10.2 Concentrating the Extract

10.2.1 Concentration by K-D

10.2.1.1 Assemble a Kuderna-Danish (K-D) apparatus by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D. If other concentration devices or techniques are used, samples processed using these devices or techniques must meet all the sample technical acceptance criteria established by the SOW.

10.2.1.2 For water sample extracts prepared as described in Section 10.1.3, pour the extract through a drying column containing about 10 cm of anhydrous granular sodium sulfate and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and the column with at least two additional 20 to 30 mL portions of methylene chloride to complete the quantitative transfer.

10.2.1.2 Low level soil/sediment/solid sample extracts prepared by the procedure described in Section 10.1.4.4 will result in extracts containing a mixture of acetone and methylene chloride. Because all soil/sediment/solid sample extracts MUST be subjected to GPC cleanup prior to analysis, the majority of the acetone must be removed from the extract. The presence of acetone will cause a dead volume to develop in the GPC column and thus will cause loss of surrogates and analytes during GPC cleanups. Transfer the extract directly to the K-D concentrator. Rinse the Erlenmeyer flask with 20-30 mL of methylene chloride to complete the quantitative transfer.

10.2.1.3 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL methylene chloride to the top of the column. Place the K-D apparatus in a hot water bath (60 °C to 70 °C recommended) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. At the proper rate of distillation, the balls of the column will chatter actively, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 or 2 mL of methylene chloride.

10.2.1.4 For water samples which do not require GPC cleanup, proceed to final concentration of extract (Section 10.2.2).

10.2.1.5 Water samples that have been found to contain higher molecular weight contaminants that interfere with the analysis of the target analytes and oily sludge (waste) samples require GPC. Adjust the final volume of the extract to 10.0 mL with methylene chloride and proceed with GPC cleanup (Section 10.3).

10.2.1.6 For soil/sediment/solid samples, it is absolutely necessary to further reduce the volume of the extract to 1.0 mL following Section 10.2.2.2 in order to ensure removal of the acetone prior to GPC cleanup. Adjust the final volume of the extract to 10.0 mL with methylene chloride, and proceed with GPC cleanup (Section 10.3).

10.2.2 Final Concentration of Extract

Two different concentration techniques are permitted to obtain the final extract volume: Micro Snyder column and Nitrogen Evaporation Techniques.

10.2.2.1 Micro Snyder Column Technique

Add another one or two clean boiling chips to the concentrator tube and attach a two-ball micro Snyder column. Pre-wet the Snyder column by adding about 0.5 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (60 °C to 70 °C recommended) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation, the balls of the column will chatter actively, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 0.5 mL (0.4 mL for soil/sediment samples or water samples that have undergone GPC), remove the K-D apparatus from the water bath and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse the evaporative flask and its lower joint into the concentrator tube with 0.2 mL (0.1 mL for soil/sediment samples or water samples that have undergone GPC) of methylene chloride. Adjust the final extract volume to the volume specified for particular matrices in Section 10.2.2.3.

10.2.2.2 Nitrogen Evaporation Technique (taken from ASTM Method D 3086)

10.2.2.2.1 Place the concentrator tube in a warm water bath (30 °C to 35 °C recommended) and evaporate the solvent volume to just below the final volume by blowing a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon) onto the solvent. The internal wall of the concentrator tube must be rinsed down several times with methylene chloride during the operation. During evaporation, the tube solvent level must be kept below the water level of the bath. DO NOT ALLOW THE EXTRACT TO GO TO DRYNESS. Remove the Snyder column and rinse the evaporative flask and its lower joint into the concentrator tube with methylene chloride. Adjust the final extract volume

to the volume specified for particular matrices in Section 10.2.2.3.

10.2.2.2.2 Gas lines from the gas source to the evaporation apparatus must be stainless steel, copper, or Teflon tubing. Plastic tubing must not be used between the carbon trap and the sample as it may introduce interferences. The internal walls of new tubing must be rinsed several times with hexane and then dried prior to use.

10.2.2.3 Final Extract Volumes

10.2.2.3.1 Water Samples

For water samples that did not undergo GPC (Section 10.3), the extract must be brought to a final volume of 1.0 mL with methylene chloride. For oily water samples that underwent GPC, the extract must be brought to a final volume of 0.5 mL with methylene chloride. (Concentrating the extract to 0.5 mL will result in no loss of sensitivity despite the volume of extract (5 mL) not recovered after GPC.)

10.2.2.3.2 Low and Medium Soil/Sediment/Solid Samples

Adjust the final extract volume to 0.5 mL with methylene chloride (concentrating the extract to 0.5 mL will result in no loss of sensitivity despite the volume of extract (5 mL) not recovered after GPC).

10.2.2.3.3 Oily Sludges(Waste)

If possible, adjust the final volume of oily sludge samples to 5.0 ml of methylene chloride (concentrating the extract to 5.0 mL will result in the original 1:10 dilution and no loss of sensitivity despite the volume of extract (5 mL) not recovered after GPC).

If the oily sludge extract cannot be concentrated to 5.0 ml after GPC cleanup, then the Contractor shall contact the RSCC for directions. The Contractor shall note any problems, the EPA sample numbers for the affected samples and the Regional instructions in the SDG Narrative.

10.2.2.3.4 Transfer the individual extract(s) to Teflon-sealed screw-cap bottle(s) or crimp cap vial(s), label the bottle(s), and store at 4 °C (±2 °C) until GC/MS analysis.

10.3 Sample Cleanup by GPC

10.3.1 Introduction

10.3.1.1 Gel Permeation Chromatography (GPC) is a size exclusion cleanup procedure using organic solvents and hydrophobic gels in the separation of natural macromolecules. The packing gel is porous and is characterized by the range or uniformity (exclusion range) of that pore size. In the choice of gels, the exclusion range must be larger than the molecular size of the molecules to be separated.

10.3.1.2 GPC must be performed for all low and medium level soil/sediment/solid extracts and for all oily sludge waste dilutions. GPC must be performed for water extracts that contain higher molecular weight contaminants that interfere with the analysis of the target analytes.

10.3.2 GPC Column Preparation

The instructions listed below for GPC column preparation are for Bio Beads. Alternative column packings may be used if 1) the column packings have equivalent or better performance than the Bio Beads and meet the technical acceptance criteria for GPC calibration (Section 10.3.4), 2) the column packings do not introduce contaminants/artifacts into the sample which interfere with the analysis of the semivolatile compounds. Follow the manufacturer's instructions for

preparation of the GPC column packing. If alternate column packings are used, samples processed through these packings must meet all the sample technical acceptance criteria established by the SOW.

10.3.2.1 Weigh out 70 g of Bio Beads (SX-3). Transfer them to a quart bottle with a Teflon-lined cap or a 500 mL separatory funnel with a large bore stopcock, and add approximately 300 mL of methylene chloride. Swirl the container to ensure the wetting of all beads. Allow the beads to swell for a minimum of 2 hours. Maintain enough solvent to cover the beads sufficiently at all times. If a guard column is to be used, repeat the above with 5 g of Bio Beads in a 125 mL bottle or a beaker using 25 mL of the methylene chloride.

10.3.2.2 Turn the column upside down from its normal position, and remove the inlet bed support plunger (the inlet plunger is longer than the outlet plunger). Position and tighten the outlet bed support plunger as near the end as possible, but no closer than 5 cm (measured from the gel packing to the collar).

10.3.2.3 Raise the end of the outlet tube to keep the solvent in the GPC column, or close the column outlet stopcock. Place a small amount of solvent in the column to minimize the formation of air bubbles at the base of poured column packing.

10.3.2.4 Swirl the bead/solvent slurry to get a homogeneous mixture and, if the wetting was done in a quart bottle, quickly transfer it to a 500 mL separatory funnel with a large bore stopcock. Drain the excess methylene chloride directly into the waste beaker, and then start draining the slurry into the column by placing the separatory funnel tip against the column wall. This will help to minimize bubble formation. Swirl occasionally to keep the slurry homogeneous. Drain enough to fill the column. Place the tubing from the column outlet into a waste beaker below the column, open the stopcock (if attached), and allow the excess solvent to drain. Raise the tube to stop the flow, and close the stopcock when the top of the gel begins to look dry. Add additional methylene chloride to just rewet the gel.

10.3.2.5 Wipe any remaining beads and solvent from the inner walls of the top of the column with a laboratory tissue. Loosen the seal slightly on the other plunger assembly (long plunger) and insert it into the column. Make the seal just tight enough so that any beads on the glass surface will be pushed forward, but loose enough so that the plunger can be pushed forward.

CAUTION: Do not tighten the seal if beads are between the seal and the glass surface because this can damage the seal and cause leakage.

10.3.2.6 Compress the column as much as possible without applying excessive force. Loosen the seal and gradually pull out the plunger. Rinse and wipe off the plunger. Slurry any remaining beads and transfer them into the column. Repeat the step in Section 10.3.2.5 and reinsert the plunger. If the plunger cannot be inserted and pushed in without allowing beads to escape around the seal, continue compression of the beads without tightening the seal, and loosen and remove the plunger as described. Repeat this procedure until the plunger is inserted successfully.

10.3.2.7 Push the plunger until it meets the gel, then compress the column bed about four centimeters.

10.3.2.8 Pack the optional 5 cm column with approximately 5 g of pre-swelled beads (different guard columns may require different amounts). Connect the guard column to the inlet of the analytical column.

10.3.2.9 Connect the column inlet to the solvent reservoir (reservoir should be placed higher than the top of the column) and place the column outlet tube in a waste container. Placing a restrictor in the outlet tube will force air out of the column more quickly. A restrictor can be made from a piece of capillary stainless steel

tubing of 1/16" OD x 0.010" ID x 2". Pump methylene chloride through the column at a rate of 5 mL/min for one hour.

10.3.2.10 After washing the column for at least one hour, connect the column outlet tube without the restrictor, to the inlet side of the UV detector. Connect the system outlet to the outlet side of the UV detector. A restrictor (same size as the one in Section 10.3.2.9) in the outlet tube from the UV detector will prevent bubble formation which causes a noisy UV baseline.

10.3.2.11 The restrictor will not affect flow rate. After pumping methylene chloride through the column for an additional 1-2 hours, adjust the inlet bed support plunger until approximately 6-10 psi backpressure is achieved. Push the plunger in to increase pressure or slowly pull outward to reduce pressure.

10.3.2.12 When the GPC column is not to be used for several days, connect the column outlet line to the column inlet to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, re-swelled, and re-poured as described above. If drying occurs, methylene chloride should be pumped through the column until the observed column pressure is constant and the column appears wet. The GPC column must be recalibrated after column drying has occurred to verify retention volumes have not changed.

10.3.3 Calibration of GPC

10.3.3.1 Summary of GPC Calibration

The GPC calibration procedure is based on monitoring the elution of standards with a UV detector connected to the GPC column.

10.3.3.2 Frequency of GPC Calibration

Calibrate the GPC system using the GPC calibration solution prepared as described in Section 7.2.4.3. Each GPC system must be initially calibrated upon award of a contract, when the column is changed, when channeling occurs, when column drying has occurred and once every seven days when samples, including QC samples and blanks are cleaned up using GPC. The Contractor may choose to calibrate the GPC system on a daily basis to ensure adequate sample collection.

10.3.3.3 Procedure for GPC Calibration

The following instructions are for the Analytical Biochemical Laboratories system. If you are using a different GPC system, consult your manufacturer's instruction manual for operating instructions. A 2 mL injection loop may be used in place of a 5 mL injection loop, in accordance with the manufacturer's instructions.

10.3.3.3.1 Verify the flow rate by collecting column eluate for 10 minutes in a graduated cylinder and measure the volume, which should be 45-55 mL (4.5-5.5 mL/min). Once the flow rate is within the range of 4.5-5.5 mL/min, record the column pressure (should be 6-10 psi) and room temperature on daily instrument logs. Changes in pressure, solvent flow rate, and temperature conditions can affect analyte retention times and must be monitored.

10.3.3.3.2 Using a 10 mL syringe, load sample loop #1 with calibration solution (Section 7.2.4.3). With the ABC automated system, the 5 mL sample loop requires a minimum of 8 mL of the calibration solution. Use a firm continuous pressure to push the sample onto the loop. Switch the valve so that GPC flow is through the UV flow-through cell.

10.3.3.3.3 Inject the calibration solution and obtain a UV trace showing a discrete peak for each component. Adjust the detector and/or recorder sensitivity to produce a UV trace that meets the requirements in Section 10.3.4. Differences between manufacturer's cell volumes and detector sensitivities may require a dilution of the calibration solution to achieve similar results. An analytical flow-through detector cell will require a much less concentrated solution than the semi-prep cell and, therefore, the analytical flow-through detector cell is not acceptable for use.

10.3.3.3.4 Using the information from the UV trace, establish appropriate COLLECT and DUMP time periods to ensure collection of all target semivolatile analytes. Initiate column eluate collection just before the elution of bis(2-ethylhexyl) phthalate and just after the elution of corn oil. Stop eluate collection shortly after the elution of perylene. If sulfur was added, collection should be stopped before sulfur elutes. Use a WASH time of 10 minutes after the elution of sulfur.

NOTE: The DUMP and COLLECT times must be adjusted to compensate for the difference in volume of the lines between the detector and the collection flask. Each laboratory is required to establish its specific time sequences.

10.3.3.3.5 Reinject the calibration solution after appropriate collect and dump cycles have been set, and the solvent flow and column pressure have been established.

10.3.3.3.6 Measure the volume of collected GPC eluate in a graduated cylinder and record the volume on the daily instrument log.

Changes in the volume of GPC eluate collected for each sample extract processed indicate potential problems with the GPC system during sample processing. See Section 10.4.4.9 for corrective actions.

10.3.3.3.7 Process and analyze a GPC blank with each SDG by loading 5 mL of methylene chloride into the GPC. Concentrate the methylene chloride that passes through the system during the collect cycle using a Kuderna-Danish (K-D) evaporator (Section 10.2.1). The final volume of the GPC blank must be the same as samples processed in the same SDG. Add internal standards at the appropriate concentration and analyze the extract by GC/MS (Section 10.6).

10.3.4 Technical Acceptance Criteria for GPC Calibration

10.3.4.1 The GPC system must be calibrated at the frequency described in Section 10.3.3.2. The UV trace must meet the following requirements:

- All peaks must be observed and must be symmetrical for all compounds in the calibration solution.
- Corn oil and the phthalate peaks must exhibit > 85.0 percent resolution.
- The phthalate and methoxychlor peaks must exhibit > 85.0 percent resolution.
- Methoxychlor and perylene peaks must exhibit > 85.0 percent resolution.
- Perylene and sulfur peaks must not be saturated and must exhibit > 90.0 percent resolution.

The percent resolution is calculated using the following equation:

$$\%Resolution = \frac{V}{H} \times 100$$

EQ. 6

Where,

V = Depth of the valley between the two peaks. The depth of the valley is measured along a vertical line from the level of the apex of the shorter peak to the floor of the valley between the two peaks.

H = Height of the shorter of the adjacent peaks from baseline.

10.3.4.2 The solvent flow rate and column pressure must be within the ranges described in Section 10.3.3.3.1.

10.3.4.3 Calculate and record on the GPC instrument log the retention time shifts between GPC calibrations. If the retention time shift between the present calibration UV trace and the last calibration UV trace is > 5.0 percent for any of the components of the GPC calibration solution, the Contractor must take the corrective action steps outlined in Section 10.3.5. Excessive retention time shifts are caused by the following:

- Poor laboratory temperature control or system leaks.
- An unstabilized column that requires pumping methylene chloride through it for several hours or overnight.
- Excessive laboratory temperatures causing outgassing of the methylene chloride.

10.3.4.4 Copies of the UV traces of the present calibration and the most recent previous calibration and the GPC instrument logs must be submitted with the data for the associated samples in each SDG submission.

10.3.4.5 The analyte concentrations in the GPC blank (Section 10.3.3.3.7) must contain less than the CRQL for all target compounds in Exhibit C (Semivolatiles), except phthalate esters, for which the GPC blank must contain less than 5 times the CRQL.

10.3.5 Corrective Action for GPC Calibration

10.3.5.1 If any of the technical acceptance criteria in Section 10.3.4 cannot be met, the first corrective action step must be to clean the column. The column is cleaned by processing several 5 mL volumes of butylchloride through the system. Butylchloride removes the discoloration and particles that may have precipitated out of the methylene chloride extracts. If a guard column is being used, replace it with a new one. This may correct the problem. If column maintenance does not restore the performance of the column, then the column must be repacked with new Bio Beads and recalibrated. It may be necessary to obtain a new lot of Bio Beads if the column continues to fail all GPC technical acceptance criteria.

10.3.5.2 If the GPC blank exceeds the requirements in 10.3.4.5, the GPC system is contaminated. Pump additional methylene chloride through the system for 1-2 hours. Analyze another GPC blank as described in Section 10.3.3.3.7 to ensure the system is sufficiently clean. If the GPC system still shows signs of contamination, repeat the methylene chloride pumping step until the GPC blank meets the GPC blank technical acceptance criteria (section 10.3.4.5) or it may be necessary to take the steps outlined in Section 10.3.5.1 above to clean the column.

10.4 Sample Extract Cleanup by GPC

10.4.1 It is very important to have constant laboratory temperatures during an entire GPC run, which could last 24 hours or more. If temperatures are not constant, retention times will shift, and the dump and collect times determined by the calibration standard no longer will be appropriate. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 22 °C.

10.4.2 In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Similarly, extracts containing more than 40 mg/mL of nonvolatile residue must be diluted and loaded into several loops. The nonvolatile residue may be determined by evaporating a 100 µL aliquot of the extract to dryness in a tared aluminum weighing pan, or other suitable container. Systems using automated injection devices to load the sample on the column must be carefully monitored to assure that the required amount is being injected on the column. Viscous extracts or extracts containing a large amount of non-volatile residue will cause problems with an automated injection system's ability to inject the proper amount of sample extract on a column. After the sample extract has been processed, the remaining sample extract in the injection vial must be checked before proceeding with extract cleanup to assure that the proper amount was injected on the column. If the proper amount of extract was not injected, the sample must be re-prepared at no additional cost to the Agency, and the sample extract must either be diluted and loaded into several loops or the sample extract must be injected manually.

Note: When multiple loops/runs are necessary for an individual sample, be sure to combine all of the sample eluates collected from each run.

10.4.3 Frequency of GPC Sample Cleanup

GPC cleanup must be performed once for each low and medium soil/sediment/solid and oily sludge (waste) extract and for water extracts that contain high molecular weight contaminants that interfere with the analysis of the target analytes. In addition, GPC

must be performed for all associated blanks and QC samples. If the GPC cleanup procedure is found to be inadequate for the sample matrix, contact the RSCC for instructions.

10.4.4 Procedure for GPC Sample Cleanup

10.4.4.1 Particles greater than 5 microns may scratch the valve, which may result in a system leak and cross contamination of sample extracts in the sample loops. To avoid such problems, filter the extract through a 5 micron filter disc by attaching a syringe filter assembly containing the filter disc to a 10 mL syringe. Draw the sample extract through the filter assembly and into the 10 mL syringe. Disconnect the filter assembly before transferring the sample extract into a small glass container, e.g., a 15 mL culture tube with a Teflon-lined screw cap. Alternatively draw the extract into the syringe without the filter assembly. Attach the filter assembly and force the extract through the filter and into the glass container. Draw a minimum of 8 mL of extract into a 10 mL syringe.

Note: Some GPC instrument manufacturers recommend using a smaller micron size filter. Follow the manufacturer's recommended operating instructions.

10.4.4.2 Introduction of particulates or glass wool into the GPC switching valves may require factory repair of the apparatus.

10.4.4.3 The following instructions are for the Analytical Biochemical Laboratories system. If a different GPC system is being used, consult the manufacturer's instruction manual for operating instructions. A 2 mL injection loop may be used in place of a 5 mL injection loop. If a 2 mL injection loop is used, concentrate the sample extract to 4 mL instead of 10 mL and then inject 2 mL instead of 5 mL.

10.4.4.4. Prior to loading samples, put the GPC into the LOAD mode, set the instrument terminal for the number of loops to be loaded, and set the DUMP, COLLECT, and WASH times for the values determined by the calibration procedure described in Section 10.3.3.3.

10.4.4.5 Using a 10 mL syringe, load the sample into the system. With the ABC automated system, the 5 mL loop requires a minimum of 8 mL of sample. Attach the syringe to the turn lock on the injection port. Use firm, continuous pressure to push the sample onto the 5 mL sample loop. If the sample is difficult to load, some part of the system may be blocked. Take appropriate corrective action. If the back pressure is normal (6-10 psi), the blockage is probably in the valve. Blockage may be flushed out of the valve by reversing the inlet and outlet tubes and pumping solvent through the tubes (this should be done before sample loading). NOTE: Approximately 2 mL of the extract remains in the lines between the injection port and the sample loop; excess sample also passes through the sample loop to waste.

10.4.4.6 After loading a loop, and before removing the syringe from the injection port, index the GPC to the next loop. This will prevent loss of sample caused by unequal pressure in the loops. After loading each sample loop, wash the loading port with methylene chloride in a PTFE wash bottle to minimize cross-contamination. Inject approximately 10 mL of methylene chloride to rinse the common tubes.

10.4.4.7 After loading all the sample loops, index the GPC to 00 position, switch to the RUN mode and start the automated sequence. Process each sample using the COLLECT and DUMP cycle time established in Section 10.3.3.3.

10.4.4.8 GPC column pressure and room temperature must be monitored throughout the GPC run. Column pressure and room temperature must be recorded in the GPC instrument log book at the following frequency: Prior to the analysis of the first sample, mid way through sample analysis and after the last sample is collected.

10.4.4.9 Collect each sample in a 250 mL Erlenmeyer flask, covered with aluminum foil to reduce solvent evaporation, or directly into a Kuderna-Danish (K-D) evaporator. Sample volumes must be monitored as they are collected and must be consistent with collection volumes established during GPC calibration (Section 10.3.3.6). Sample volumes must be recorded in the GPC instrument log book. Changes in sample volumes collected may indicate one or more of the following problems with the GPC system:

- Change in solvent flow rate, caused by channeling in the column or changes in column pressure.
- Increase in column operating pressure due to the absorption of particles or gel fines onto either the guard column or the analytical column gel, if a guard column is mut used.
- Leaks in the system or significant variances in room temperature.

Any discrepancies noted during GPC cleanup and necessary corrective actions must be included in the SDG Narrative.

10.5 Final Concentration

Concentrate the GPC extracts as per Section 10.2.2. Final extract volumes for specific matrices are specified in Section 10.2.2.3.

10.6 Sample Analysis by GC/MS

10.6.1 Sample extracts shall be analyzed only after the GC/MS system has met the GC/MS instrument performance check, initial calibration, initial calibration verification, continuing calibration and required blank technical acceptance criteria (Section 9.0). The same GC/MS instrument conditions must be used for the analysis of samples as were used for calibration.

10.6.2 Internal standard solution is added to each sample, blank and QC sample extract. Add 10 µL of internal standard solution (Section 7.2.4.5) to each accurately measured 1.0 mL water sample extract. For all low/medium soil/sediment/solid samples and water samples subjected to GPC, add 5 µL of internal standard solution to each accurately measured 0.5 mL of sample extract. For oily sludge (waste) samples (final volume 5.0 mL), add 5 µL of internal standard solution to each accurately measured 0.5 mL aliquot of the sample extract. This will result in a concentration of 20 ng/µL of each internal standard.

10.6.3 If sample dilutions are necessary to achieve the sample technical acceptance criteria, additional internal standard solution must be added to maintain the required 20 ng/µL of each internal standard in the extract volume.

10.6.4 Inject 2 µL of each sample, blank and QC sample extract into the GC/MS. This 2 µL volume must contain 40 ng of each internal standard.

10.6.5 Sample Dilutions

10.6.5.1 If the on-column concentration of any compound in any sample exceeds the initial calibration range, that sample extract must be diluted, the internal standard concentration must be readjusted to 20 ng/µl, and the diluted sample extract must be analyzed. Guidance in performing dilutions and exceptions to this requirement are given below.

10.6.5.2 Use the results of the original analysis to determine the approximate dilution factor required to get the largest target compound peak within the initial calibration range.

10.6.5.3 The dilution factor chosen should keep the response of the largest peak for a target compound in the upper half of the calibration range of the instrument.

10.6.5.4 Do not submit data for more than two analyses, i.e., the original sample extract and one dilution, or if the semivolatile screening procedure was employed, from the most concentrated dilution analyzed and one further dilution.

10.6.5.5 The Contractor may receive instructions with the sampling paperwork which prohibits sample dilutions under any circumstances. This may be required in instances where the CRQLs for most target compounds must be achieved even though one or more target compounds exceed the calibration range and/or high concentrations of non-target compounds are present. In these cases, if screening results indicate that sample dilution is required to avoid detector saturation due to target and/or non-target compound ions, then the contractor shall contact the RSCC to ascertain whether or not that sample should be analyzed at a dilution. For all samples affected by this situation, the Contractor shall note the problem, the EPA sample numbers affected by this situation, and the Regional instructions in the SDG Narrative.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Identification

11.1.1 Identification of Target Compounds

11.1.1.1 The compounds listed in the Target Compound List (TCL), Exhibit C (Semivolatile), shall be identified by an analyst competent in the interpretation of mass spectra (see Exhibit A) by comparison of the sample mass spectrum to the mass spectrum of the standard of the suspected compound. Two criteria must be satisfied to verify the identifications.

- Elution of the sample component at the same GC relative retention time as the 12-hour calibration standard component.
- Correspondence of the sample component and calibration standard component mass spectra.

11.1.1.2 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ±0.06 RRT units of the RRT of the standard component. For reference, the standard must be run in the same 12-hour time period as the sample. If samples are analyzed during the same 12-hour time period as the initial calibration standards, compare the analyte retention times to those from the 50 ng calibration standard. If co-elution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

11.1.1.3 For comparison of standard and sample component mass spectra, mass spectra obtained from a calibration standard on the Contractor's GC/MS are required. Once obtained, these standard spectra may be used for identification purposes, only if the contractor's GC/MS meets the daily GC/MS instrument performance check technical acceptance criteria. These standard spectra must be obtained from the run used to obtain reference RRTs.

11.1.1.4 The requirement for qualitative verification by comparison of mass spectra are as follows:

- All ions present in the standard mass spectrum at a relative intensity greater than 10.0 percent (most abundant ion in the spectrum equals 100.0 percent) **must** be present in the sample spectrum.
- The relative intensities of ions specified above must agree within ± 20.0 percent between the standard and sample spectrum. (Example: For an ion with an abundance of 50.0 percent in the standard spectrum, the corresponding sample ion abundance must be between 30.0 and 70.0 percent).
- Ions greater than 10.0 percent in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. All compounds meeting the identification criteria must be reported with their spectra. When target compounds are detected below contract required quantitation limits (CRQL) but the spectrum meets the identification criteria, report the concentration with a "J". For example, if the CRQL is 10 µg/L and a concentration of 3 µg/L is calculated, report as "3J" µg/L.

11.1.1.5 If a compound cannot be verified by all of the criteria in Section 11.1.1 (11.1.1.1 through 11.1.1.4) but, in the technical judgement of the mass spectra interpretation specialist, the identification is correct, then the contractor shall report the identification on the Form I - SV qualified with an "X". The Contractor must note this decision in the SDG narrative and proceed with quantitation as described in Section 11.2.

11.1.2 Identification of Non-Target Compounds

11.1.2.1 A library search shall be executed for non-target sample components for the purpose of tentative identification. For this purpose, the NIST/EPA/NIH (May 1992 release or most recent release) and/or Wiley (1991 release or most recent release), or equivalent mass spectral library shall be used.

11.1.2.2 Up to 10 organic compounds of greatest apparent concentration not listed in Exhibit C for the volatile and semivolatile fraction, excluding the surrogate and internal standard compounds, shall be identified tentatively via a forward search of the NIST/EPA/NIH (May 1992 release or most recent release) and/or Wiley (1991 release or most recent release), or equivalent mass spectral library. The following are not to be reported: 1) Substances with responses less than 10 percent of the internal standard (as determined by inspection of the peak areas or heights); 2) substances which elute earlier than 30 seconds before the first semivolatile compound listed in Exhibit C (Semivolatiles) or three minutes after the last semivolatile compound listed in Exhibit C has eluted; and 3) volatile compounds (TCL VOA) listed in Exhibit C (Volatiles). The mass spectral interpretation specialist will assign a tentative identification only after visual comparison of the sample spectrum with all the library search spectra.

11.1.2.3 Peaks that are suspected to be aldol-condensation reaction products (i.e., 4-methyl-4-hydroxy-2-pentanone and 4-methyl-3-pentene-2-one) shall be searched and reported but are **not** counted as part of the 10 most intense non-target semivolatile compounds. When the above aldol-condensation reaction products are tentatively identified, the concentration(s) are to be estimated as described in Section 11.2.2 and reported on the Form I SV-TIC qualified with an "A".

11.1.2.4 NOTE: Computer generated library search routines must not use normalizations which would misrepresent the library or unknown spectra when compared to each other.

11.1.2.5 Guidelines for Making Tentative Identifications

11.1.2.5.1 Relative intensities of major ions in the reference spectrum (ions greater than 10 percent of the most abundant ion) should be present in the sample spectrum.

11.1.2.5.2 The relative intensities of the major ions should agree within ± 20 percent of the reference and sample spectrum (Example: For an ion with an abundance of 50 percent in the reference spectrum, the corresponding sample ion abundance must be between 30 and 70 percent).

11.1.2.5.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

11.1.2.5.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

11.1.2.5.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting compounds. Data system library reduction programs sometimes can create these discrepancies.

11.1.2.5.6 If, in the technical judgement of the mass spectral interpretation specialist, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral interpretation specialist should give additional classification of the unknown compound, if possible (i.e., unknown phthalate, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, then the mass spectral interpretation specialist should include them on the Form I SV - TIC and provide discussion in the SDG Narrative.

11.1.2.5.7 The Contractor shall report any pesticide target compounds listed in Exhibit C (Pesticides) that are identified as

semivolatile tentatively identified compounds. These compounds should be reported on the Form I SV - TIC and the presence of these compounds should be noted in the SDG Narrative.

11.2 Calculations

11.2.1 Target Compounds

11.2.1.1 Target compounds which meet the identification criteria in Section 11.1.1 shall be quantitated by the internal standard method. The internal standard used shall be the one assigned to that analyte for quantitation (see Table 2). The EICP area of primary characteristic ions of analytes listed in Tables 3 and 4 are used for quantitation.

11.2.1.2 The relative response factor (RRF) from the continuing calibration standard is used to calculate the concentration in the sample. For samples analyzed during the same 12-hour time period as the initial calibration standards, use the RRF values from the 50 ng calibration standard. Secondary ion quantitation is allowed ONLY when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, document the reason and the EPA sample number in the SDG Narrative. A secondary ion cannot be used unless a relative response factor is calculated using that secondary ion.

11.2.1.3 Calculate the concentration in the sample using the daily 12 hour relative response factor (RRF) and the following equations.

11.2.1.3.1 Water

EQ. 7

$$Concentration\ \mu g/L = \frac{(A_x)(I_s)(V_t)(Df)(GPC)}{(A_{is})(RRF)(V_o)(V_i)}$$

Where,

A_x = Area of the characteristic ion (EICP) for the compound to be measured

A_{is} = Area of the characteristic ion (EICP) for the internal standard

I_s = Amount of internal standard injected in nanograms (ng)

V_o = Volume of water extracted in milliliters (mL)

V_i = Volume of extract injected in microliters (µL)

V_t = Volume of the concentrated extract in microliters (µL) (V_t = 1,000 µL if sample was not subjected to GPC; V_t = 500 µL if sample was subjected to GPC)

RRF = Relative response factor determined from the 12-hour calibration standard

GPC = GPC factor.
GPC = 1.0 if water sample was not subjected to GPC;
GPC = 2.0 if water sample was subjected to GPC.

Df = Dilution factor. The dilution factor for semivolatile analysis of water samples by this method is defined as follows:

$$\frac{\text{µL most concentrated extract + µL clean solvent}}{\text{µL most concentrated extract}}$$

If no dilution is performed, Df = 1.0.

11.2.1.3.2 Low/Medium Soil/Sediment/Solid Samples and Oily Sludge (Waste)

EQ. 8

$$Concentration\ \mu g/Kg\ (Dry\ weight\ basis) = \frac{(A_x)(I_s)(V_t)(Df)(GPC)}{(A_{is})(RRF)(V_i)(W_s)(D)}$$

Where,

A_x, I_s, A_{is} and RRF are as given for water, above.

V_t = Volume of the concentrated extract in microliters (µL) (V_t = 500 µL for Soil/Sediment/Solid, V_t = 5,000 µL for Oily Sludge (Waste))

V_i = Volume of the extract injected in microliters (µL)

$D = \frac{100 - \%\ moisture}{100}$

W_s = Weight of sample extracted in grams (g)

GPC = GPC factor (GPC = 2.0 to account for GPC cleanup)

Df = Dilution factor. The dilution factor for semivolatile analysis of soil/sediment/solid or oily sludge (waste) samples by this method is defined as follows:

$$\frac{\mu L\ most\ concentrated\ extract + \mu L\ clean\ solvent}{\mu L\ most\ concentrated\ extract}$$

If no dilution is performed, Df= 1.0

The factor of 2.0 in the numerator is used to account for the amount of extract that is not recovered from the mandatory use of GPC cleanup. Concentrating the extract collected after GPC to 0.5 mL for low/medium soil/sediment/solid samples maintains the sensitivity of the method, while concentrating the extract to 5.0 mL for oily sludge (waste) samples maintains the original waste dilution of 1:10.

11.2.1.4 It is expected that situations will arise where the automated quantitation procedures in the GC/MS software provide inappropriate quantitations. This normally occurs when there is compound co-elution, baseline noise, or matrix interferences. In these circumstances, the Contractor must perform a manual quantitation. Manual quantitations are performed by integrating the area of the quantitation ion of the compound. This integration shall only include the area attributable to the specific TCL compound. The area integrated shall not include baseline background noise. The area integrated shall not extend past the point where the sides of the peak intersect with the baseline noise. Manual integration is not to be used solely to meet QC criteria, nor is it to be used as a substitute for corrective action on the chromatographic system. Any instance of manual integration must be documented in the SDG Narrative and flagged on the quantitation report.

11.2.1.5 In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the GC/MS operator must identify such edits or manual procedures by initialing and dating the changes made to the report, and must include the integration scan range on the quantitation report. In addition, a hardcopy printout of the EICP of the quantitation ion displaying the manual integration shall be included in the raw data. This applies to all compounds listed in Exhibit C (Semivolatiles), internal standards and surrogates.

11.2.1.6 The requirements listed in 11.2.1.4 and 11.2.1.5 apply to all standards, samples, QC samples and blanks.

11.2.2 Non-Target Compounds

11.2.2.1 An estimated concentration for non-target compounds tentatively identified shall be quantitated by the internal standard method.

For quantitation, the nearest internal standard free of interferences shall be used.

11.2.2.2 The equations for calculating concentration are the same as equations 7 and 8. Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. A relative response factor (RRF) of one (1) is to be assumed. The resulting concentration shall be qualified as "J" (estimated, due to lack of a compound specific response factor), and "N" (presumptive evidence of presence), indicating the quantitative and qualitative uncertainties associated with this non-target component. An estimated concentration should be calculated for all tentatively identified compounds as well as those identified as unknowns.

11.2.3 CRQL Calculations

Sample specific CRQLs must be calculated and reported on Form I SV. If the adjusted CRQL is less than the CRQL in Exhibit C (Semi-volatiles), report the CRQL listed in Exhibit C (Semivolatiles).

11.2.3.1 Water Samples

EQ. 9

$$\underset{CRQL}{Adjusted} = \underset{CRQL}{Contract} \times \frac{(V_x)(V_t)(V_y)(Df)}{(V_o)(V_c)(V_i)}$$

Where,

V_t, Df, V_o and V_i are as given in equation 7.
V_x = Contract sample volume (1,000 mL)
V_y = Contract injection volume (2 µL)
V_c = Contract concentrated extract volume (1,000 µL if GPC is not performed, and 500 µL if GPC was performed).

11.2.3.2 Low/Medium Soil/Sediment/Solid or Oily Sludge (Waste) Samples

EQ. 10

$$\underset{CRQL}{Adjusted} = \underset{CRQL}{Contract} \times \frac{(W_x)(V_t)(V_y)(Df)}{(W_s)(V_c)(V_i)(D)}$$

Where,

V_t, Df, W_s, V_i and D are as given in equation 8.
W_x = Contract sample weight (30 g for low level and 1 g for medium level soil/sediment and oily sludge (waste) samples)
V_y = Contract injection volume (2 µL)
V_c = Contract concentrated extract volume (500 µL for soil/sediment/solid samples and 5,000 µL for oily sludge (waste) samples, GPC is required).

11.2.4 Surrogate Recoveries

11.2.4.1 Calculate the concentrations of the surrogate compounds in all samples, QC samples and blanks using the same equations as used for the target compounds (Section 11.2.1).

11.2.4.2 Calculate the surrogate recovery in all samples, QC samples and blanks using Equation 11, below. Determine if percent recovery (% R) is within the surrogate recovery limits listed in Table 7 and report the %Rs on Form II SV as specified in Exhibit B.

EQ. 11

$$\%Recovery = \frac{Concentration\ (or\ amount)\ found}{Concentration\ (or\ amount)\ spiked} \times 100$$

11.2.5 Internal Standard Responses and Retention Times

The extracted ion current profile (EICP) of the internal standards and their retention times in all samples, QC samples and blanks must be monitored and evaluated during or immediately after data acquisition. Compare sample internal standard responses and retention times to the continuing calibration internal standard responses and retention times. For samples analyzed during the same 12-hour time period as the initial calibration standards, compare the internal standard responses and retention times against the 50 µg/µL calibration standard. The internal standard responses and retention times for all samples, QC samples and blanks are summarized on Form VIII SV for each 12 hour time period.

11.3 Technical Acceptance Criteria for Sample Analysis

Target and non target compounds in samples are identified and reported following procedures defined in Sections 11.1 and 11.2. Sample technical acceptance criteria must be met before any sample data can be reported.

11.3.1 The samples must be analyzed on a GC/MS system meeting the GC/MS Instrument Performance Check, initial calibration, initial calibration verification and/or continuing calibration technical acceptance criteria. The sample must undergo cleanup procedures, when required, on a GPC meeting the technical acceptance criteria for GPC calibration (Section 10.3.4).

11.3.2 The sample must be extracted and analyzed or reextracted and reananlyzed within the contract holding times defined in Section 8.3.

11.3.3 The sample must have an associated method blank(s) meeting the blank technical acceptance criteria defined in Section 12.1.4.

11.3.4 The sample must have surrogate recoveries within the recovery limits defined in Table 7 . The sample surrogate recoveries will be considered unacceptable if the following occurs:

- Any surrogate has a recovery less than 10.0 percent.
- More than one base neutral surrogate or more than one acid surrogate is outside the surrogate recovery limits listed in Table 7.

NOTE: These requirements do not apply to surrogates with advisory windows and to dilutions of samples.

11.3.5 The relative retention time of each surrogate must be within ± 0.06 RRT units of its relative retention time in the most recent continuing calibration standard.

11.3.6 The response (EICP area) for each of the internal standards must be within the inclusive range of -50.0 percent and +100.0 percent of the EICP area of the internal standards in the most recent continuing calibration analysis.

11.3.7 The retention time shift for each of the internal standards must be within ± 0.50 minutes (30 seconds) between the sample's internal standard retention times and the most recent continuing calibration standard's internal standard retention times.

11.3.8 Excluding those ions in the solvent front, no ion from a target or non-target compound may saturate the detector. No target compound concentration may exceed the upper limit of the 12-hour standard calibration range unless a more dilute aliquot of the sample extract is also analyzed according to the procedures in Section 10.6.5.

11.4 Corrective Action for Sample Analysis

11.4.1 The sample technical acceptance criteria must be met before data are reported. Samples contaminated from laboratory sources, or sample results submitted not meeting the sample technical acceptance criteria, will require re-extraction and/or reanalysis at no additional cost to the Agency.

11.4.2 Corrective actions for failure to meet GC/MS instrument performance check, initial and continuing calibration and initial calibration verification must be completed before the analysis of samples.

11.4.3 Corrective actions for failure to meet blank technical acceptance criteria must be met before the analysis of any samples.

11.4.4 Corrective actions for surrogate recoveries which fail to meet the recovery limits (Section 11.3.4, Table 7) are defined below.

11.4.4.1 If any of the surrogate compounds fail to meet their recovery acceptance criteria:

- Check all calculations, sample preparation logs, the surrogate compound spiking solutions, and the instrument operation. If the calculations were incorrect, correct the calculations and verify that the surrogate compound recoveries meet their recovery limits.
- If the sample preparation logs indicate that the incorrect amount of surrogate compound spiking solution was added, then re-extract and reanalyze the sample after adding the correct amount of surrogate spiking solution.
- If the surrogate compound spiking solution was improperly prepared or, has concentrated or degraded, re-prepare the solutions and re-extract/reanalyze the samples.
- If the surrogate recoveries were outside the lower surrogate acceptance limit and the extract from the sample was cleaned up on a GPC using an automated injection system, the Contractor shall verify that the proper amount was injected on the GPC column. If insufficient sample volume was injected on

the GPC, the sample must be reprepared and reanalyzed at no additional cost to the Agency.

- If the GC/MS instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. Verify that the surrogate recoveries meet their recovery limits. If the instrument malfunction affected the calibrations, recalibrate the instrument before reanalyzing the sample extract.

- If low surrogate recoveries occur in aqueous samples and it does not appear to be either a GPC or GC/MS instrument malfunction, then assure that 1) the liquid-liquid extraction apparatus was properly assembled to prevent leaks; 2) the drip rate/solvent cycling of the extraction apparatus was optimized; and 3) there was proper cooling for condensation of solvent (Section 10.1.3).

11.4.4.2 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was matrix effect, take the following corrective action steps.

11.4.4.2.1 Re-extract and reanalyze the sample. EXCEPTION: If the surrogate compound recoveries in a sample used for a matrix spike and/or matrix spike duplicate were considered unacceptable, then the sample should be re-extracted/reanalyzed only if surrogate compound recoveries met the surrogate recovery limits in both the matrix spike and matrix spike duplicate analysis.

11.4.4.2.2 If the surrogate compound recoveries meet the recovery limits in the re-extracted/reanalyzed sample, then the problem was within the Contractor's control. Therefore, submit only data from the re-extraction/reanalysis.

11.4.4.2.3 If the surrogate compound recoveries fail to meet the recovery limits in the re-extracted/reanalyzed sample, then submit data from both analyses. Distinguish between the initial analysis and the re-extraction/reanalysis on all deliverables, using the suffixes in Exhibit B.

11.4.5 Corrective Actions for internal standard compound EICP area responses which fail to meet their technical acceptance criteria (Section 11.3.6) are defined below.

11.4.5.1 If any of the internal standard responses fail to meet their technical acceptance criteria:

- Check calculations, the internal standard compound spiking solution and the GC/MS instrument operation. If the calculations were incorrect, correct the calculations and verify that the internal standard response met their technical acceptance criteria.

- If the internal standard compound spiking solution was improperly prepared or has concentrated or degraded, re-prepare the internal standard spiking solution and re-extract/reanalyze the affected samples.

- If the GC/MS instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. If the GC/MS instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extracts.

11.4.5.2 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was matrix effect, take the following corrective action steps:

11.4.5.2.1 Reanalyze the sample extract. EXCEPTION: If internal standard compound responses in a sample used for a matrix spike and/or matrix spike duplicate were outside the acceptance windows, then the sample should be reanalyzed only if internal standard compound responses met the internal standard response acceptance criteria in both the matrix spike and matrix spike duplicate analysis.

11.4.5.2.2 If the internal standard compound responses meet the technical acceptance criteria in the reanalyzed sample extract, then the problem was within the Contractor's control. Therefore, submit only data from the reanalysis.

11.4.5.2.3 If the internal standard compound responses fail to meet their acceptance windows in the reanalyzed sample extract, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables, using the suffixes in Exhibit B.

11.4.6 Corrective actions for surrogate compound relative retention times/internal standard compound retention times outside technical acceptance criteria (Sections 11.3.5 and 11.3.7) are defined below:

11.4.6.1 If the surrogate compounds relative retention times or internal standard compounds retention times are not within their technical acceptance criteria, check the GC/MS instrument for malfunctions. If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extracts. If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extracts.

11.4.6.2 If the above actions do not correct the problem, then the problem may be due to a sample "matrix effect". To determine if there was a matrix effect, take the following corrective action steps:

11.4.6.2.1 Reanalyze the sample extract. EXCEPTION: If the surrogate compounds relative retention times or internal standard compounds retention times in a sample used for a matrix spike and/or matrix spike duplicate were outside the technical acceptance criteria, then it should be reanalyzed only if the surrogate compounds relative retention times and internal standard compounds retention times were within the acceptance criteria in both the matrix spike and matrix spike duplicate analysis.

11.4.6.2.2 If the surrogate compounds relative retention times and internal standard compounds retention times are within the technical acceptance criteria in the reanalyzed sample extract, then the problem was within the Contractor's control. Therefore, submit only data from the compliant reanalysis with the surrogate compounds relative retention times and the internal standard compound retention times within the acceptance limits. If the sample was reanalyzed outside the contract required holding times, then submit both sets of data.

11.4.6.2.3 If the surrogate compounds relative retention times or internal standard compounds retention times are outside the technical acceptance criteria in the reanalyzed sample extract, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables, using the suffixes in Exhibit B.

11.4.7 If the technical acceptance criteria for GC/MS instrument performance checks, initial and continuing calibration, initial calibration verification and/or method blanks are not met, then the contractor must stop and correct the problem before continuing the analytical sequence. Any samples analyzed when the above technical acceptance criteria have not been met must be reanalyzed at no additional cost to the agency. Reanalysis must be completed within the contract required holding times and must meet all technical acceptance criteria.

11.4.8 Sample analyses reported with non-compliant GC/MS instrument performance check, initial and/or continuing calibration, initial calibration verification or method blanks shall be subject to a commensurate reduction in sample price or zero payment due to data rejection, depending upon the impact of the non-compliance on data usability.

12.0 QUALITY CONTROL

12.1 Method Blanks

12.1.1 Summary of Method Blanks

A method blank is a volume of a clean reference matrix (reagent water for water samples, purified sodium sulfate for low and medium soil/sediment/solid samples that is carried through the entire analytical procedure. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of a method blank is to determine the level(s) of contamination, if any, associated with the processing and analysis of samples.

12.1.2 Frequency of Method Blanks

Method blank extraction and analysis must be performed once for the following, whichever is most frequent, and analyzed on each GC/MS system used to analyze associated samples:

- Each SDG, or
- Each 20 samples in an SDG, including QC samples, that are of a similar matrix (water, soil/sediment/solid, oily sludge) or similar concentration (soil/sediment only), or
- Whenever samples are extracted by the same procedure (continuous liquid-liquid extraction, sonication or waste dilution).

12.1.3 Procedure for Method Blank Preparation

For semivolatile analyses, a method blank for water samples consists of a 1 L volume of reagent water spiked with 0.5 mL of the surrogate spiking solution (Section 7.2.4.1.2). For medium and low level soil/sediment/solid samples, a method blank consists of l g and 30 g of sodium sulfate, respectively, spiked with 0.5 mL of the surrogate spiking solution (Section 7.2.4.1.2). For oily sludge (waste) samples, a method blank consists of 9.0 mL of methylene chloride spiked with 1.0 mL of concentrated surrogate spiking solution (Section 7.2.4.1.3). Extract, concentrate, cleanup, analyze and report the method blank according to procedures for water and soil samples (Sections 10.0 and 11.0).

12.1.4 Technical Acceptance Criteria for Method Blank Analysis

12.1.4.1 All blanks must be extracted and analyzed on a GC/MS system meeting the GC/MS Instrument Performance Check, initial calibration, initial calibration verification and/or continuing calibration technical acceptance criteria at the frequency described in Section 12.1.2. A GPC blank must also be prepared and analyzed with each set of samples which are cleaned up using GPC (Section 10.3.3.3.7).

12.1.4.2 The blank(s) must meet all sample analysis technical acceptance criteria defined in Section 11.3.

12.1.4.3 The concentration of each target compound found in the method and/or GPC blanks must be less than its CRQL listed in Exhibit C (semivolatiles), except for the phthalate esters, which must be less than five times (5x) their respective CRQLs.

12.1.4.4 Non-target compounds which are found in the blanks must not interfere with target compound identification or quantitation.

12.1.5 Corrective Action for Method Blanks

12.1.5.1 If a Contractor's method blank exceeds the technical acceptance criteria for method blank analysis in Section 12.1.4.3, the Contractor shall consider the entire analytical system to be out of control.

12.1.5.2 If contamination is the problem, then the source of the contamination must be investigated and appropriate corrective action measures must be taken and documented before further sample analysis proceeds. It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvent, reagents, glassware, and sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in the GC/MS be eliminated. Samples associated with the contaminated blank must be reextracted and reanalyzed at no additional cost to the Agency.

12.1.5.3 If surrogate recoveries (except those with advisory limits) in the method blank do not meet the recovery limits listed in Table 7, first reanalyze the method blank. If the surrogate recoveries do not meet the recovery limits after reanalysis, follow the corrective actions for surrogate recoveries in samples outlined in Section 11.4.4. If corrective actions do not resolve the problem, the method blank and all samples associated with that method blank must be reextracted and reanalyzed at no additional cost to the Agency.

12.1.5.4 If the method blank does not meet internal standard response requirements for samples listed in 11.2.5, follow the corrective actions for internal standard responses in samples outlined in Section 11.4.5. If corrective actions do not resolve the problem, the method blank and all samples associated with that method blank must be reextracted and reanalyzed at no additional cost to the Agency.

12.1.5.5 If the method blank does not meet the retention time requirements for internal standards (11.3.7) or the surrogate compounds (11.3.5), follow the corrective actions for retention time requirements in samples outlined in Section 11.4.6. Reanalyze the method blank. If corrective actions do not resolve the problem, the method blank and all samples associated with that method blank must be reextracted and reanalyzed at no additional cost to the Agency.

12.1.5.6 If the technical acceptance criteria (Section 12.1.4) for blank analyses are not met, then the contractor must stop and correct the problem before continuing the analytical sequence. If sample analyses are reported with non-compliant blanks, then the contractor may receive a commensurate reduction in sample price or zero payment depending upon the impact of the non-compliance on data usability.

12.2 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

12.2.1 Summary of MS/MSD

In order to evaluate the effects of the sample matrix on the methods used for semivolatile analyses, the Agency has prescribed a mixture of semivolatile target compounds to be spiked into two aliquots of a sample and analyzed in accordance with the appropriate method.

12.2.2 Frequency of MS/MSD Analyses

12.2.2.1 A matrix spike and matrix spike duplicate must be performed for each group of samples of a similar matrix for the following, whichever is most frequent:

- Each SDG (not to exceed 20 field samples), or
- Each matrix within an SDG, or
- Each group of samples of a similar concentration level (soils only).
- EPA may require additional MS/MSD analyses, upon Regional request, for which the Contractor will be paid.

12.2.2.2 As part of the Agency's QA/QC program, aqueous equipment rinsate blanks (field QC) may accompany soil/sediment/solid samples, water samples and/or oily sludge (waste) samples that are delivered to the laboratory for analysis. The Contractor shall not perform MS/MSD analysis on any of the field QC samples.

12.2.2.3 The Contractor shall not perform MS/MSD analysis on any designated Performance Evaluation (PE) samples.

12.2.2.4 If the EPA Region designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample volume remaining to perform an MS/MSD, then the Contractor shall contact the RSCC to ascertain an alternate sample to be used for the MS/MSD analysis. The EPA sample numbers, Regional instructions and date of contact must be included in the SDG Narrative.

12.2.2.5 If there is insufficient sample volume remaining in any of the samples in an SDG to perform an MS/MSD, then the Contractor shall immediately contact the RSCC to report the problem. The Region will either approve that no MS/MSD is required, or require that a reduced sample aliquot be used for the unspiked sample and MS/MSD analysis. The RSCC will notify the Contractor of the resolution. The Contractor shall document the decision in the SDG Narrative.

12.2.2.6 If the Contractor has a question regarding the frequency, etc., of the MS/MSD analyses for a particular SDG, contact the RSCC for clarification.

12.2.3 Procedure for Preparing MS/MSD

12.2.3.1 Water Samples

For water samples, prepare two additional 1 L aliquots of the sample chosen for spiking in two continuous extractors. Add 0.5 mL of the surrogate standard spiking solution (Section 7.2.4.1.2) and 0.5 mL of the matrix spiking solution (Section 7.2.4.2.2) to each sample aliquot. Extract, concentrate, cleanup, and analyze the MS/MSD according to the procedures for water samples (Section 10.1.3).

12.2.3.2 Soil/Sediment/Solid Samples - Low Level

For low level soil/sediment/solid samples, prepare two additional 30 g aliquots (record weight to nearest 0.1 g) of the sample chosen for spiking in the two 400 mL beakers. Add 60 g of anhydrous powdered sodium sulfate to each aliquot. Mix well. Add 0.5 mL of the surrogate standard spiking solution (Section 7.2.4.1.2) and 0.5 mL of the matrix spiking solution (Section 7.2.4.2.2) to each sample aliquot, then immediately add 100 mL of 1:1 methylene chloride-acetone. Extract, concentrate, cleanup, and analyze the MS/MSD according to the procedures for low level soil/sediment/solid samples (Section 10.1.4.4).

12.2.3.3 Soil/Sediment/Solid Samples - Medium Level

For medium level soil/sediment/solid samples, prepare two additional 1 g aliquots (record weight to nearest 0.1 g) of the sample chosen for spiking in two 20 mL vials. Add 2.0 g of anhydrous powdered sodium sulfate to each sample aliquot. Mix well. Add 0.5 mL of the surrogate standard spiking solution (Section 7.2.4.1.2), 0.5 mL of the matrix spiking solution (Section 7.2.4.2.2), and 9.0 mL of methylene chloride. Extract, concentrate, cleanup, and analyze the MS/MSD according to the procedures for medium level soil/sediment/solid samples (Section 10.1.4.5).

12.2.3.4 Oily Sludge Samples - Waste Dilution

For oily sludge (waste) samples, prepare two additional 1 g aliquots (record weight to the nearest 0.1 g) of the sample chosen for spiking in two precalibrated 20 mL vials. Add 2.0 g of anhydrous powdered sodium sulfate to each sample aliquot and mix well. Add 1.0 mL of the more concentrated surrogate standard spiking solution (Section 7.2.4.1.3) and 1.0 mL of the more concentrated matrix spiking solution (Section 7.2.4.2.3) to each sample aliquot. Mix well and dilute to 10.0 mL with methylene chloride. Extract, cleanup and analyze the MS/MSD according to procedures for oily sludge samples (Section 10.1.4.6).

12.2.4 Dilution of MS/MSD

Before any MS/MSD analysis, analyze the original sample, then analyze the MS/MSD at the same concentration as the most concentrated extract for which the original sample results will be reported. For example, if the original sample is to be reported at a 1:1 dilution and a 1:10 dilution, then analyze and report the MS/MSD at a 1:1 dilution only. However, if the original sample is to be reported at a 1:10 dilution and a 1:100 dilution, then the MS/MSD must be analyzed and reported at a 1:10 dilution only. Do <u>not</u> further dilute the MS/MSD samples to get either spiked or non-spiked analytes within calibration range.

Dilution of the sample must be performed in accordance with the conditions for sample dilutions specified in Section 10.6.5.

12.2.5 Calculations for MS/MSD

12.2.5.1 Calculate the concentrations of the matrix spike compounds using the same equations used to calculate target compounds (Section 11.2.1).

12.2.5.2 Calculate the recovery of each matrix spike compound using the following equation:

EQ. 12

$$Matrix\ Spike\ Recovery = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.2.5.2 Calculate the relative percent difference (RPD) of the recoveries of each compound in the matrix spike and matrix spike duplicate as follows:

EQ. 13

$$RPD = \frac{|MSR - MSDR|}{\frac{1}{2}(MSR + MSDR)} \times 100$$

Where,

RPD = Relative Percent Difference
MSR = Matrix Spike Recovery
MSDR = Matrix Spike Duplicate Recovery

The vertical bars in the formula above indicate the absolute value of the difference, hence RPD is always expressed as a positive value.

12.2.6 Technical Acceptance Criteria for MS/MSD

12.2.6.1 All MS/MSDs must be analyzed on a GC/MS system meeting the GC/MS instrument performance check, initial calibration, initial calibration verification, continuing calibration and method blank technical acceptance criteria. The MS/MSD must undergo cleanup procedures, when required, on a GPC meeting the technical acceptance criteria for GPC calibration. All MS/MSDs must be prepared and analyzed at the frequency described in Section 12.2.2.

12.2.6.2 The MS/MSDs must be extracted and analyzed or reextracted and reananlyzed within the contract holding time specified in Section 8.3.

12.2.6.3 The MS/MSDs must meet all sample technical acceptance criteria defined in Sections 11.3.4 through 11.3.8.

12.2.6.4 The limits for matrix spike/matrix spike duplicate compound recoveries and RPD are given in Table 6. As these limits are only advisory, no further action by the laboratory is required. However, frequent failures to meet the limits for MS/MSD recoveries or RPD, warrant investigation by the laboratory and may result in questioning from the Agency.

12.2.7 Corrective Action for MS/MSD

Any MS/MSD that does not meet the technical acceptance criteria for MS/MSD must be reanalyzed at no additional cost to the Agency. Both sets of data must be reported.

12.2.7.1 Corrective actions for failure to meet GC/MS instrument performance check, initial and continuing calibration and initial calibration verification must be completed before the analysis of any QC samples.

12.2.7.2 Corrective actions for failure to meet blank technical acceptance criteria must be met before the analysis of any QC samples.

12.2.7.3 Corrective actions for surrogate recoveries defined in Section 11.4.4 and/or internal standard compound responses defined in

Section 11.4.5 must be completed before QC sample results are reported.

12.2.7.4 Corrective actions for surrogate relative retention times and/or internal standard compound retention times defined in Section 11.4.6 must be completed before QC sample results are reported.

12.2.7.5 If the technical acceptance criteria for MS/MSD analysis are not met, the contractor shall determine whether the non-compliance is due to the sample matrix or GC/MS system problems.

12.2.7.6 If the non-compliance is found to be due to a sample matrix effect, take the following corrective action steps:

- Reanalyze the sample. EXCEPTION: If surrogate recoveries or internal standard compound responses in a sample used for a matrix spike or matrix spike duplicate were outside the technical acceptance criteria, then it should be reanalyzed only if the surrogate recoveries and internal standard compound responses met acceptance criteria in both the matrix spike and matrix spike duplicate analyses.

- If the MS/MSD recoveries/RPD meet the MS/MSD technical acceptance criteria in the reanalyzed sample, then the problem was within the Contractor's control. The contractor should make every effort to reanalyze the sample within the contract required holding times. If the reanalysis was performed within holding times, then submit data only from the reanalysis. If the reanalysis was performed outside holding times, then submit both sets of data.

- If the MS/MSD recoveries/RPD fail to meet the acceptance criteria in the reanalysis, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables using the suffixes in Exhibit B.

12.3 SDG-Specific Performance Evaluation (PE) Samples

12.3.1 Summary of SDG-Specific PE Samples

The Region I Performance Evaluation (PE) program has two functions: (1) to evaluate laboratory operation and protocols over a period of time, and (2) to provide information on the quality of individual data packages.

12.3.2 Frequency of SDG-Specific PE Samples

12.3.2.1 The Region will submit PE samples with every SDG per parameter, matrix and concentration level (as available). The Region may obtain these SDG-Specific PE samples from either a commercial vendor or from the CLP National Program Office (NPO) which provides PE samples in support of the Superfund program. PE samples provided by the CLP-NPO are referred to as "EPA-generated".

12.3.2.2 When the Region submits aqueous trip and/or equipment blanks and/or Performance Evaluation samples (PEs) with soil/sediment/solid field samples, then the Contractor shall not perform an MS/MSD analysis on the aqueous matrix (trip blank, equipment blank, PE sample). When the Region submits an aqueous PE sample with aqueous field samples, then the Contractor shall not choose the PE sample for MS/MSD analysis.

12.3.2.3 If the PE sample is received as an ampulated standard extract, the ampulated PE sample is not considered to be another matrix type.

12.3.3 Procedure for Preparing SDG-Specific PE Samples

12.3.3.1 Instructions for preparation of the PE samples will be included with each submission of PE samples.

12.3.3.2 If PE sample directions do not apply to a PE sample received, then the Contractor must contact the RSCC to ascertain whether or not

to analyze the PE sample and to obtain appropriate PE sample directions.

12.3.4 Calculations for SDG-Specific PE Samples

12.3.4.1 For EPA-generated and commercially prepared PE samples that are submitted with each SDG, the Contractor must correctly identify and quantitate all TCL compounds in the PE sample using the criteria presented in Section 11.0 - Data Analysis and Calculations.

12.3.5 Technical Acceptance Criteria for SDG Specific PE Samples

12.3.5.1 All SDG-Specific PE samples must be analyzed under the same GC/MS conditions set up in Section 9.0 and must meet the same technical acceptance criteria established for sample analysis defined in Section 11.3.

12.3.5.2 EPA-generated PE samples included with the SDG will be evaluated by the Region using a CLP NPO computer program called Peac TOOLs. Peac TOOLs rates the PE sample results based on statistically generated confidence intervals.

12.3.5.3 The results of commercially prepared PE samples will be evaluated using the vendors' statistically generated confidence intervals.

12.3.5.4 Contractor results for the SDG-Specific PE samples will be evaluated using the most recent Region I data validation criteria for PE samples.

12.3.5.5 At a minimum, the PE results will be evaluated for compound identification, quantitation, and sample contamination. Confidence intervals for the quantitation of target compounds are based on reported values using population statistics. The Agency may adjust the scores on any given laboratory PE sample to compensate for unanticipated difficulties with a particular sample. Normally, a fraction of the compounds spiked into the sample are not specifically listed in the contract. Contractors must use the guidelines described in Section 11.1.2 for identification of non-target compounds. Tentative identification of these non-target compounds is reviewed and integrated into the evaluation process.

12.3.6 Corrective Action for SDG-Specific PE Samples

12.3.6.1 The corrective actions for PE sample results which do not meet the technical acceptance criteria defined in Section 12.3.5.1 above are the same corrective actions outlined for sample analysis in Section 11.4.

12.3.6.2 If an SDG-Specific PE sample evaluated by Region I as described in Sections 12.3.5.2 through 12.3.5.6 above, indicates unacceptable laboratory performance, then the Contractor may be required to reanalyze all samples, standards, blanks and QC samples associated with the unacceptable PE sample result (if sufficient volume remains) and/or analyze a new PE sample at no additional cost to the Agency. Unacceptable laboratory performance includes either a TCL false positive result, false negative result, and/or compound misquantitation (reported result exceeds $\pm$ 3 sigma of the spiked compound concentration).

12.3.6.3 SDG-Specific sample results reported with unacceptable PE results shall be subject to a commensurate reduction in sample price or zero payment due to data rejection, depending upon the impact of the non-compliance on data usability.

12.4 CLP Quarterly Blind (QB) Laboratory Evaluation Program

12.4.1 Summary of CLP QB Samples

The Region will also submit quarterly laboratory evaluation samples for specified analyses in conjunction with the CLP Quarterly Blind (QB) program. The results from the analysis of these QB samples will

be used by the Region to verify the Contractor's continuing ability to produce acceptable analytical data. The results will also be used to assess the precision and accuracy of the analytical methods.

12.4.2 Frequency of CLP QB Samples

12.4.2.1 The Region will submit laboratory evaluation samples on a quarterly basis for specified analyses in conjunction with the CLP Quarterly Blind (QB) program.

12.4.3 Procedure for Preparing CLP QB Samples

12.4.3.1 Instructions for preparation of the QB samples will be included with each submission of QB samples.

12.4.4 Calculations for CLP QB Samples

12.4.4.1 The Contractor must correctly identify and quantitate all TCL compounds in the QB sample using the criteria presented in Section 11.0 - Data Analysis and Calculations.

12.4.5 Technical Acceptance Criteria for CLP QB Samples

12.4.5.1 The QB samples must be analyzed under the same GC/MS conditions set up in Section 9.0 and must meet the same technical acceptance criteria established for sample analysis defined in Section 11.3.

12.4.5.2 The QB samples will be scored and the results will be used to assess the precision and accuracy of the analytical methods.

12.4.5.3 At a minimum, the QB results are evaluated for compound identification, quantitation, and sample contamination. Confidence intervals for the quantitation of target compounds are based on reported values using population statistics. The Agency may adjust the scores on any given laboratory evaluation sample to compensate for unanticipated difficulties with a particular sample. Normally, a fraction of the compounds spiked into the sample are not specifically listed in the contract. Contractors must use the guidelines described in Section 11.1.2 for identification of non-target compounds. Tentative identification of these non-target compounds is reviewed and integrated into the evaluation process.

12.4.5.4 The Contractor's performance on the QB samples will be measured and reported as follows:

12.4.5.4.1 Acceptable, No Response Required (Score greater than or equal to 90%): Data meets most or all of the scoring criteria.

12.4.5.4.2 Acceptable, Response Explaining Deficiency(ies) Required (Score greater than or equal to 75% but less than 90%): Deficiencies exist in the Contractor's performance.

12.4.5.4.3 Unacceptable Performance (Score less than 75%): Deficiencies exist in the Contractor's performance to the extent that the Agency has determined that the Contractor has not demonstrated the capability to meet the contract requirements.

12.4.5.4.4 In the case of Sections 12.4.5.4.2 and 12.4.5.4.3 above, the Contractor shall respond to the deficiency(ies) and the action(s) taken to correct the deficiency(ies) in a letter to the Contract Officer and the Project Officer, within 14 days of receipt of notification from the Agency.

12.4.6 Corrective Action for CLP QB Samples

12.4.6.1 The corrective actions for QB sample results which do not meet the technical acceptance criteria defined in Section 12.4.5.1 above are the same corrective actions outlined for sample analysis in Section 11.4.

12.4.6.2 After receipt and review of the Contractor's deficiency letter (Section 12.4.5.4.4), the Agency will notify the Contractor concerning the remedy for their unacceptable performance. The Contractor may expect, but the Agency is not limited to, the

following actions: commensurate reduction in sample price, zero payment due to data rejection, reduction of the number of samples sent under the contract, suspension of sample shipment to the Contractor, a GC/MS tape audit, a data package audit, an on-site laboratory evaluation, a remedial laboratory evaluation sample, and/or contract sanctions, such as a Cure Notice.

NOTE: The Contractor's prompt response demonstrating that corrective actions have been taken to ensure the Contractor's capability to meet contract requirements may facilitate continuation of sample scheduling.

13.0 METHOD PERFORMANCE

Not Applicable.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When it is not feasible to reduce waste at the source, the Agency recommends recycling as the next best option.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistently with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions.

16.0 REFERENCES

Not Applicable.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Table 1

DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30.0 - 80.0 percent of mass 198
68	Less than 2.0 percent of mass 69
69	Present
70	Less than 2.0 percent of mass 69
127	25.0 - 75.0 percent of mass 198
197	Less than 1.0 percent of mass 198
198	Base peak, 100 percent relative abundance (see Note)
199	5.0 - 9.0 percent of mass 198
275	10.0 - 30.0 percent of mass 198
365	Greater than 0.75 percent of mass 198
441	Present but less than mass 443
442	40.0 - 110.0 percent of mass 198
443	15.0 - 24.0 percent of mass 442

Note: All ion abundances MUST be normalized to m/z 198, the nominal base peak, even though the ion abundance of m/z 442 may be up to 110 percent that of m/z 198.

Table 2

Semivolatile Internal Standards With Corresponding
Target Compounds and Surrogates Assigned for Quantitation

1,4-Dichlorobenzene-d	Naphthalene-d_8	Acenaphthene-d_{10}	Phenanthrene-d	Chrysene-d_{12}	Perylene-d_{12}
Phenol	Nitrobenzene	Hexachlorocyclo-pentadiene	4,6-Dinitro-2-methylphenol	Pyrene	Di-n-octyl-phthalate
bis(2-Chloroethyl) ether	Isophorone	2,4,6-Trichloro-phenol	N-nitroso-di-phenylamine	Butylbenzyl-phthalate	Benzo(b)fluor-anthene
2-Chlorophenol	2-Nitrophenol	2,4,5-Trichloro-phenol	4-Bromophenyl phenolether	3,3'-Dichloro-benzidine	Benzo(k)fluor-anthene
1,3-Dichlorobenzene	2,4-Dimethyl-phenol	2-Chloronaph-thalene	Hexachloro-benzene	Benzo(a)-anthracene	Benzo(a)pyrene
1,4-Dichlorobenzene	bis(2-Chloro-ethoxy)methane	2-Nitroaniline	Pentachloro-phenol	bis(2-ethyl-hexyl)phthalate	Indeno(1,2,3-cd)-pyrene
1,2-Dichlorobenzene	2,4-Dichloro-phenol	Dimethyl-phthalate	Carbazole	Chrysene	Benzo(g,h,i)-perylene
2-Methylphenol	1,2,4-Trichlo-robenzene	Acenaphthylene	Phenanthrene	di(2-ethyl hexyl)adipate	Dibenzo(a,h)-anthracene
2,2'-oxybis-(1-Chloropropane)	Naphthalene	3-Nitroaniline	Anthracene	Terphenyl-d_{14} (surr)	
4-Methylphenol	4-Chloroanaline	Acenaphthene	Di-n-butyl-phthalate		
N-Nitroso-Di-n-propylamine	Hexachloro-butadiene	2,4-Dinitro-phenol	Fluoranthene		
Hexachloroethane	4-Chloro-3-methylphenol	4-Nitrophenol	2,4,6-Tri-bromophenol (surr)		
2-Fluorophenol (surr)	2-Methylnaph-thalene	Dibenzofuran			
Phenol-d_5 (surr)	Nitrobenzene-d_5 (surr)	2,4-Dinitrotoluene			
2-Chlorophenol-d_4 (surr)		2,6-Dinitrotoluene			
1,2-Dichlorobenzene-d_4 (surr)		Diethylphthalate			
		4-Chlorophenyl-phenylether			
		Fluorene			
		4-Nitroaniline			
		2-Fluorobiphenyl (surr)			

surr = surrogate compound

Table 3

Characteristic Ions for Internal Standards
for Semivolatile Compounds

INTERNAL STANDARDS	Primary Quantitation Ion	Secondary Ions
1,4-Dichlorobenzene-d4	152	115
Naphthalene-d8	136	68
Acenaphthene-d10	164	162, 160
Phenanthrene-d10	188	94, 80
Chrysene-d12	240	120, 236
Perylene-d12	264	260, 265

Table 4

Characteristic Ions for Semivolatile
Target Compounds and Surrogates

Parameter	Primary Quantitation Ion	Secondary Ion(s)
Phenol	94	65, 66
bis(2-Chloroethyl)ether	93	63, 95
2-Chlorophenol	128	64, 130
1,3-Dichlorobenzene	146	148, 113
1,4-Dichlorobenzene	146	148, 113
1,2-Dichlorobenzene	146	148, 113
2-Methylphenol	108	107
2,2'-oxybis(1-Chloropropane)	45	77, 79
4-Methylphenol	108	107
N-Nitroso-di-n-propylamine	70	42, 101, 130
Hexachloroethane	117	201, 199
Nitrobenzene	77	123, 65
Isophorone	82	95, 138
2-Nitrophenol	139	65, 109
2,4-Dimethylphenol	107	121, 122
bis(2-Chloroethoxy)methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
1,2,4-Trichlorobenzene	180	182, 145
Naphthalene	128	129, 127
4-Chloroaniline	127	129
Hexachlorobutadiene	225	223, 227
4-Chloro-3-methylphenol	107	144, 142
2-Methylnaphthalene	142	141
Hexachlorocyclopentadiene	237	235, 272
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 200
2-Chloronaphthalene	162	164, 127
2-Nitroaniline	65	92, 138
Dimethyl phthalate	163	194, 164
Acenaphthylene	152	151, 153
3-Nitroaniline	138	108, 92
Acenaphthene	153	152, 154
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	109	139, 65
Dibenzofuran	168	139
2,4-Dinitrotoluene	165	63, 182
2,6-Dinitrotoluene	165	89, 121
Diethylphthalate	149	177, 150
4-Chlorophenyl-phenylether	204	206, 141
Fluorene	166	165, 167
4-Nitroaniline	138	92, 108
4,6-Dinitro-2-methylphenol	198	182, 77

Table 4 (cont'd.)

Characteristic Ions for Semivolatile
Target Compounds and Surrogates

Parameter	Primary Quantitation Ion	Secondary Ion(s)
N-Nitrosodiphenylamine	169	168, 167
4-Bromophenyl-phenylether	248	250, 141
Hexachlorobenzene	284	142, 249
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	179, 176
Carbazole	167	166, 139
Di-n-butylphthalate	149	150, 104
Fluoranthene	202	101, 100
Pyrene	202	101, 100
Butylbenzylphthalate	149	91, 206
3,3'-Dichlorobenzidine	252	254, 126
Benzo(a)anthracene	228	229, 226
bis(2-ethylhexyl)phthalate	149	167, 279
di(2-ethylhexyl)adipate	57	55, 129
Chrysene	228	226, 229
Di-n-Octyl phthalate	149	---
Benzo(b)fluoranthene	252	253, 125
Benzo(k)fluoranthene	252	253, 125
Benzo(a)pyrene	252	253, 125
Indeno(1,2,3-cd)pyrene	276	138, 227
Dibenzo(a,h)anthracene	278	139, 279
Benzo(g,h,i)perylene	276	138, 277
SURROGATES		
Phenol-d5	99	42, 71
2-Fluorophenol	112	64
2,4,6-Tribromophenol	330	332, 141
Nitrobenzene-d5	82	128, 54
2-Fluorobiphenyl	172	171
Terphenyl-d14	244	122, 212
2-Chlorophenol-d4	132	68, 134
1,2-Dichlorobenzene-d4	152	115, 150

Table 5

Relative Response Factor Criteria for Initial and Continuing Calibration of Semivolatile Target Compounds and Surrogates

Semivolatile Compounds	Minimum RRF	Maximum %RSD	Maximum %Diff
Phenol	0.800	20.5	±25.0
bis(2-Chloroethyl)ether	0.700	20.5	±25.0
2-Chlorophenol	0.800	20.5	±25.0
1,3-Dichlorobenzene	0.600	20.5	±25.0
1,4-Dichlorobenzene	0.500	20.5	±25.0
1,2-Dichlorobenzene	0.400	20.5	±25.0
2-Methylphenol	0.700	20.5	±25.0
2,2'-oxybis(1-Chloropropane)	0.010	30.0	±30.0
4-Methylphenol	0.600	20.5	±25.0
N-Nitroso-di-n-propylamine	0.500	20.5	±25.0
Hexachloroethane	0.300	20.5	±25.0
Nitrobenzene	0.200	20.5	±25.0
Isophorone	0.400	20.5	±25.0
2-Nitrophenol	0.100	20.5	±25.0
2,4-Dimethylphenol	0.200	20.5	±25.0
bis(2-Chloroethoxy)methane	0.300	20.5	±25.0
2,4-Dichlorophenol	0.200	20.5	±25.0
1,2,4-Trichlorobenzene	0.200	20.5	±25.0
Naphthalene	0.700	20.5	±25.0
4-Chloroaniline	0.010	30.0	±30.0
Hexachlorobutadiene	0.010	30.0	±30.0
4-Chloro-3-methylphenol	0.200	20.5	±25.0
2-Methylnaphthalene	0.400	20.5	±25.0
Hexachlorocyclopentadiene	0.010	30.0	±30.0
2,4,6-Trichlorophenol	0.200	20.5	±25.0
2,4,5-Trichlorophenol	0.200	20.5	±25.0
2-Chloronaphthalene	0.800	20.5	±25.0
2-Nitroaniline	0.010	30.0	±30.0
Dimethylphthalate	0.010	30.0	±30.0
Acenaphthylene	0.900	20.5	±25.0
3-Nitroaniline	0.010	30.0	±30.0
2,6-Dinitrotoluene	0.200	20.5	±25.0
Acenaphthene	0.900	20.5	±25.0
2,4-Dinitrophenol	0.010	30.0	±30.0
4-Nitrophenol	0.010	30.0	±30.0
Dibenzofuran	0.800	20.5	±25.0
2,4-Dinitrotoluene	0.200	20.5	±25.0
Diethylphthalate	0.010	30.0	±30.0
4-Chlorophenyl-phenylether	0.400	20.5	±25.0
Fluorene	0.900	20.5	±25.0
4-Nitroaniline	0.010	30.0	±30.0
4,6-Dinitro-2-methylphenol	0.010	30.0	±30.0
N-Nitrosodiphenylamine	0.010	30.0	±30.0

Table 5 (cont'd.)

Relative Response Factor Criteria for Initial and Continuing Calibration of Semivolatile Target Compounds and Surrogates

Semivolatile Compounds	Minimum RRF	Maximum %RSD	Maximum %Diff
4-Bromophenyl-phenylether	0.100	20.5	±25.0
Hexachlorobenzene	0.100	20.5	±25.0
Pentachlorophenol	0.050	20.5	±25.0
Phenanthrene	0.700	20.5	±25.0
Carbazole	0.010	30.0	±30.0
Di-n-butylphthalate	0.010	30.0	±30.0
Fluoranthene	0.600	20.5	±25.0
Pyrene	0.600	20.5	±25.0
Butylbenzylphthalate	0.010	30.0	±30.0
3,3'-Dichlorobenzidine	0.010	30.0	±30.0
Benzo(a)anthracene	0.800	20.5	±25.0
bis(2-Ethylhexyl)phthalate	0.010	30.0	±30.0
di(2-ethylhexyl)adipate	0.010	30.0	±30.0
Chrysene	0.700	20.5	±25.0
Di-n-octylphthalate	0.010	30.0	±30.0
Benzo(b)fluoranthene	0.700	20.5	±25.0
Benzo(k)fluoranthene	0.700	20.5	±25.0
Benzo(a)pyrene	0.700	20.5	±25.0
Indeno(1,2,3-cd)pyrene	0.500	20.5	±25.0
Dibenzo(a,h)anthracene	0.400	20.5	±25.0
Benzo(g,h,i)perylene	0.500	20.5	±25.0
SURROGATES			
Nitrobenzene-d5	0.200	20.5	±25.0
2-Fluorobiphenyl	0.700	20.5	±25.0
Terphenyl-d14	0.500	20.5	±25.0
Phenol-d5	0.800	20.5	±25.0
2-Fluorophenol	0.600	20.5	±25.0
2,4,6-Tribromophenol	0.010	30.0	±30.0
2-Chlorophenol-d4	0.800	20.5	±25.0
1,2-Dichlorobenzene-d4	0.400	20.5	±25.0

Table 6

Matrix Spike Recovery and
Relative Percent Difference Limits

Compound	% Recovery Water	RPD Water	% Recovery Soil/ Sediment	RPD Soil/ Sediment
Phenol	12-110	42	26-90	35
2-Chlorophenol	27-123	40	25-102	50
1,4-Dichlorobenzene	36-97	28	28-104	27
N-Nitroso-di-n-propylamine	41-116	38	41-126	38
1,2,4-Trichlorobenzene	39-98	28	38-107	23
4-Chloro-3-methylphenol	23-97	42	26-103	33
Acenaphthene	46-118	31	31-137	19
4-Nitrophenol	10-80	50	11-114	50
2,4-Dinitrotoluene	24-96	38	28-89	47
Pentachlorophenol	9-103	50	17-109	47
Pyrene	26-127	31	35-142	36

Table 7

Surrogate Recovery Limits

COMPOUND	%Recovery Water	%Recovery Soil/Sediment
Nitrobenzene-d5 (Base/Neutral)	35-114	23-120
2-Fluorobiphenyl (Base/Neutral)	43-116	30-115
Terphenyl-d14 (Base/Neutral)	33-141	18-137
Phenol-d5 (Acid)	10-110	24-113
2-Fluorophenol (Acid)	21-110	25-121
2,4,6-Tribromophenol (Acid)	10-123	19-122
2-Chlorophenol-d4 (Acid)	33-110 (advisory)	20-130 (advisory)
1,2-Dichlorobenzene-d4 (Base/Neutral)	16-110 (advisory)	20-130 (advisory)

APPENDIX A - SCREENING OF SEMIVOLATILE ORGANIC EXTRACTS

1.0 SCOPE AND APPLICATION

1.1 The analytical method described in this section is designed to characterize soil/sediment samples from hazardous waste sites for the concentration level of organics.

1.2 The method involves the preparation of soil/sediment samples which may contain organic compounds at a level greater than 10,000 µg/kg and screening with a gas chromatograph equipped with a flame ionization detector (GC/FID).

1.3 For soil/sediment samples, the results of the screen are used to determine which of the two sample preparation procedures (low or medium) is required, and to determine appropriate dilution factor for GC/MS analysis. The results of the screen may also be used to assist the analyst in performing Gel Permeation Chromatography (GPC) cleanup procedures on extracts of either water or soil/sediment samples.

1.4 The procedure is designed to allow a quantitation limit for screening purposes as low as 10,000 µg/kg for extractable organics. For analysis purposes, the quantitation limit is 10,000 µg/kg for extractable organics. Some samples may contain high concentrations of compounds that interfere with the analysis of other components at lower levels; the quantitation limits in those cases may be significantly higher.

1.5 These extraction and preparation procedures were developed for rapid and safe handling of high concentration hazardous waste samples. The design of the methods thus does not stress efficient recoveries or low limits of quantitation of all components. Rather, the procedures were designed to screen, at moderate recovery and sufficient sensitivity, a broad spectrum of organic chemicals. The results of the analyses thus may reflect only a minimum of the amount actually present in some samples.

2.0 SUMMARY OF METHOD

2.1 It is mandatory that all soil/sediment samples be characterized as to concentration level so that the appropriate analytical protocol is chosen to ensure proper quantitation limits for the sample. Note that the terms "low level" and "medium level" are descriptions of the concentration ranges that are encompassed by the "low" and "medium" level procedures.

2.2 The laboratory is at liberty to select the method of characterization. The following two screening methods may be used for soil/sediment sample characterization:

- Screen an aliquot from the "low level" 30 g extract or an aliquot from the "medium level" 1 g extract.
- Screen using GC/FID as the screening instrument.

2.3 The concentration ranges covered by these two procedures may be considered to be approximately 330 µg/kg - 10,000 µg/kg for the low level analysis and >10,000 µg/kg for medium level analysis for semivolatile extractables.

2.4 Sample Preparation

2.4.1 Low Level Soil/Sediment

A 30 g portion of soil/sediment is mixed with anhydrous powdered sodium sulfate and extracted with 1:1 methylene chloride/acetone using an ultrasonic probe.
5.0 mL of the 300 mL (approximate) total extract is concentrated to 1.0 mL and screened. If the original sample concentration is >10,000 µg/Kg, the 30 g extract is discarded and the medium level preparation procedure followed.

2.4.2 Medium Level Soil/Sediment

Approximately 1 g portions of soil/sediment are transferred to vials, mixed with anhydrous powdered sodium sulfate and extracted with methylene chloride. 5.0 mL of the 10.0 mL extract is concentrated to 1.0 mL and screened. If the

sample concentration is <10,000 µg/kg the 1 g extract is discarded and the low level method is followed.

2.5 GC/FID Screening

The concentrated extracts of soil/sediment or water samples are screened on a gas chromatograph/flame ionization detector using a fused silica capillary column (FSCC) for semivolatile priority pollutants and related organics. The results of these screens will determine whether sufficient quantities of pollutants are present to warrant analysis by the medium level protocol.

3.0 INTERFERENCES

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the chromatograms. All of these materials routinely must be demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source.

4.0 SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should be made available to all personnel involved in these analyses. Specifically, concentrated sulfuric acid presents some hazards and is moderately toxic and extremely irritating to the skin and mucous membranes. Use these reagents in fume hoods whenever possible, and if eye or skin contact occurs, flush with large volumes of water.

4.2 Always wear safety glasses or a shield for eye protection, protective clothing and observe proper mixing when working with these reagents.

5.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, catalog and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of this SOW is the responsibility of the contractor.

5.1 Glassware

5.1.1 Continuous Liquid-Liquid Extractors - equipped with Teflon or glass connecting joints and stopcocks requiring no lubrications (Hershberg-Wolf Extractor, Ace Glass Company, Vineland, NJ. P/N 6841 10 or equivalent).

5.1.2 Beakers - 400 mL

5.1.3 Syringes - 0.5 mL

5.1.4 Glass Scintillation Vials - at least 20 mL, with screw cap and Teflon or aluminum foil liner.

5.1.5 Vials and Caps - 2 mL capacity for GC auto sampler.

5.1.6 Disposable Pipets - Pasteur, 1 mL

5.1.7 Drying Column - 19 mm ID chromatographic column with coarse frit (substitution of a small pad of Pyrex glass wool for the frit will prevent cross contamination of sample extracts).

5.2 Kuderna-Danish (K-D) Apparatus

5.2.1 Concentrator Tubes - 15 mL and 10 mL graduated (Kontes K-570050-1025 and 570040-1025 or equivalent). Calibrations must be checked at the volumes employed in the test. Ground-glass stoppers are used to prevent evaporation of extracts.

5.2.2 Evaporative Flasks - 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.3 Snyder Column - Two-ball Micro (Kontes K-569001-0219 or equivalent).

5.3 Spatula - stainless steel or Teflon

5.4 Balances - Analytical, capable of accurately weighing ± 0.0001 g and one capable of weighing 100 g to ± 0.01 g. The balances must be calibrated with class S weights or known reference weights once per each 12-hour work shift. The balances must be calibrated with class S weights at a minimum of once per month. The balances must also be annually checked by a certified technician.

5.5 Ultrasonic Cell Disruptors - Heat Systems, Ultrasonic Inc., Model W-385 Sonicator (475 watt with pulsing capability, No. 200, ½ inch tapped disruptor horn, No. 419 1/8 inch standard tapered Microtip probe, and No. 305, 3/4 inch tapered high gain, `Q' disruptor horn, or No. 208 3/4 inch standard solid disruptor horn), or equivalent devices with a minimum of 375 watt output capability.

NOTE: In order to ensure that sufficient energy is transferred to the sample during extraction, the Microtip probe or horn must be replaced if the tip begins to erode. Erosion of the tip is evidenced by a rough surface.

5.6 Sonabox Acoustic Enclosure - recommended with above disruptors for decreasing cavitation sound.

5.7 Vacuum Filtration Apparatus

5.7.1 Buchner Funnel

5.7.2 Filter paper - Whatmann No. 41 or equivalent

5.8 Pyrex Glass Wool - rinsed with methylene chloride.

5.9 Silicon Carbide Boiling Chips - approximately 10/40 mesh. Heat to 400 °C for 30 minutes or Soxhlet extract with methylene chloride.

5.10 Water Bath - heated, with concentric ring cover, capable of temperature control (± 2 °C). The bath should be used in a hood.

5.11 Nitrogen Evaporation Device - equipped with a water bath that can be maintained at 35 - 40 °C. (N-Evap by Organomation Associates, Inc., South Berlin, MA, or equivalent). To prevent the release of solvent fumes into the laboratory, the nitrogen evaporation device must be used in a hood.

5.12 Gas Chromatograph/Flame Ionization Detector (GC/FID System)

5.12.1 Gas Chromatograph - an analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port must be designed for on-column injection when using packed columns and for splitless injection when using capillary columns.

5.12.2 Gas Chromatograph Column - 30 m (or longer) X 0.32 mm, 1 micron film thickness, silicone coated, fused silica capillary column (J & W scientific DB-5 or equivalent). Note that this is minimum requirement for column length. Longer columns may be used.

5.12.3 Flame Ionization Detector

6.0 REAGENTS AND STANDARDS

6.1 Reagents

6.1.1 Reagent Water - defined as water in which an interferant is not observed at or above the CRQL for each analyte of interest.

6.1.2 Sodium Thiosulfate - (ACS) granular.

6.1.3 Sulfuric Acid Solution (1+1) - slowly add 50 mL of concentrated H_2S0_4 (sp.gr. 1.84) to 50 mL of reagent water.

6.1.4 Acetone, methanol, methylene chloride - pesticide residue analysis grade or equivalent.

6.1.5 Sodium Sulfate - anhydrous powdered reagent grade. Purify by heating at 400 °C for four hours in a shallow tray. Cool in a desiccator and store in a glass bottle (Baker anhydrous powder, catalog #73898 or equivalent).

6.2 Standards

6.2.1 Introduction

The contractor must provide all standard solutions to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit E. The contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the contractor and presented upon request.

6.2.2 Stock Standard Solution

6.2.2.1 Prepare or purchase a stock standard solution containing phenol, phenanthrene, and di-n-octyl phthalate at concentrations of 1 µg/µL. Prepare stock standard solutions by accurately weighing about 0.01 g of pure material. Dissolve the material in pesticide quality methylene chloride and dilute to volume in a 10 mL volumetric flask. Larger volumes may be used at the convenience of the analyst. If compound purity is assayed at 97.0 percent or greater, the weight may be used without correction to calculate the concentration of the stock standard. If the compound purity is assayed to be less than 97.0 percent, the weight must be corrected when calculating the concentration (see Exhibit E, Analytical Standards Requirements). Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source (see Exhibit E).

6.2.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Stock standard solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem.

6.2.3 Working Standard Solutions

6.2.3.1 Surrogate Standard Spiking Solution

Prepare a surrogate standard spiking solution that contains nitrobenzene-d_5, terphenyl-d_{14}, 2-fluorobiphenyl, and 1,2-dichlorobenzene-d_4 at a concentration of 100 µg/mL; phenol-d_5, 2,4,6-tribromophenol, 2-fluorophenol, and 2-chlorophenol-d_4 at a concentration of 150 µg/mL. Surrogate standards are added to all samples and calibration solutions. Additional surrogates may be added at the laboratory's discretion.

6.2.3.2 GC Calibration Standard

Prepare a working standard mixture of phenol, phenanthrene and di-n-octylphthalate. The concentration must be such that the volume injected equals 50 ng of each compound.

6.2.4 Storage of Standards

6.2.4.1 Store the stock standard solutions at less than 4 °C but not greater than 6 °C in Teflon-lined screw-cap amber bottles and protect from light.

6.2.4.2 Store the working standards at less than 4 °C but not greater than 6 °C in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after six months or sooner if comparison with quality control check samples indicates a problem.

6.2.4.3 Samples, sample extracts and standards must be stored separately.

7.0 QUALITY CONTROL

7.1 Method Blank

7.1.1 Summary

A method blank is a volume of a clean reference matrix (reagent water for water samples, or purified sodium sulfate for soil/sediment samples) that is carried through the entire analytical procedure. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

7.1.2 Frequency

One method blank must be extracted and analyzed on each GC/FID system used to screen samples for the following, whichever is most frequent.

- Each SDG, or
- Each 20 samples in a SDG, including matrix spike and re-analyses, that are of similar matrix (water, soil, or sediment) or similar concentration (soil only), or
- Whenever samples are extracted by the same procedure (continuous liquid-liquid extraction or sonication).

7.1.3 Procedure

For semivolatile analyses, a method blank for water samples consists of a 1 L volume of reagent water spiked with 0.5 mL of the surrogate spiking solution. For medium and low level soil/sediment samples, method blanks consist of 1 g and 30 g of sodium sulfate spiked with 0.5 mL of surrogate spiking solution, respectively. Extract and concentrate method blanks at the same time as the samples associated with the blanks according to Section 12.1. Analyze the method blank according to Section 12.1.

8.0 CALIBRATION AND STANDARDIZATION

8.1 GC/FID Operating Conditions

Suggested GC operating conditions are as follows:

- Initial column temperature hold - 20 °C for 4 minutes
- Column temperature program - 20-280 °C at 8 °C /minute
- Final column temperature hold -280 °C for 8 minutes
- Injector - Grob-type, splitless
- Sample volume - 1-2 µL
- Carrier gas - Helium at 30 cm/sec

8.2 GC Calibration

8.2.1 Summary

Prior to sample analysis, each GC/FID system must be initially calibrated at one concentration level to determine instrument sensitivity.

8.2.2 Frequency

Each GC/FID system must be calibrated at the beginning of each 12-hour shift.

8.2.3 Procedure

Inject 1-2 µL of the GC calibration standard prepared in Section 6.2.3.2. The volume injected must equal 50 ng of each of the calibration compounds.

8.2.4 Technical Acceptance Criteria

8.2.4.1 The GC must be standardized for half-scale response from 50 ng of phenanthrene.

8.2.4.2 The GC must adequately separate phenol from the solvent front.

8.2.4.3 A minimum of quarter-scale response for 50 ng of di-n-octylphthalate must be exhibited.

8.2.5 Corrective Action

8.2.5.1 If the technical acceptance criteria are not met, recalibrate the GC instrument. It may be necessary to change the column or take other corrective actions to achieve the acceptance criteria.

8.2.5.2 GC calibration technical acceptance criteria must be met before any samples are injected.

9.0 PROCEDURE

9.1 Sample Preparation

9.1.1 Low Level Soil/Sediment

9.1.1.1 Decant and discard any water layer on a sediment sample. Mix samples thoroughly, especially composited samples. Discard any foreign objects such as sticks leaves and rocks.

9.1.1.2 Weigh approximately 30 g of sample to the nearest 0.1 g into a 400 mL beaker and proceed with low level soil/sediment sample preparation as described in Section 10.1.4.4 of the Semivolatile Analytical Method.

9.1.1.3 Take 5 mL from the 300 mL (approximate) total extract and concentrate to 1 mL following Section 10.2.2.1 or 10.2.2.2 of Exhibit D (Semivolatiles), but note that the final volume for screening is 1 mL, not 0.5 mL.

9.1.2 Medium Level Soil/Sediment

9.1.2.1 Decant and discard any water layer on a sediment sample. Mix samples thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves and rocks.

9.1.2.2 Transfer approximately 1 g (record weight to the nearest 0.1 g) of sample to a 20 mL vial. Wipe the mouth of the vial with a tissue to remove any sample material and proceed with the medium level sample preparation procedure described in Section 10.1.4.5 of Exhibit D (Semivolatiles).

9.1.2.3 Take 5 mL from the 10 mL total extract and concentrate to 1 mL following Section 10.2.2.1 or 10.2.2.2 of Exhibit D (Semivolatiles).

9.2 GC/FID Analysis

Inject 1-2 µL of extract.

9.3 Interpretation of Chromatograms

9.3.1 Soil/Sediment

9.3.1.1 If no sample peaks from the extract (from low or medium level preparation) are detected, or all are less than 10.0 percent full scale deflection, the sample must be prepared by the low level protocol.

9.3.1.2 Peaks are detected at greater than 10.0 percent full scale deflection and less than or equal to full scale deflection.

- If the screen is from the medium level extract, proceed with GC/MS analysis of this extract with appropriate dilution if necessary.
- If the screen is from the low level extract, discard the extract and prepare the samples by medium level method for GC/MS analysis.

9.3.1.3 Peaks are detected at greater than full scale deflection.

- If the screen is from the medium level preparation, calculate the dilution necessary to reduce the major peaks to between half and full scale deflection. Use this dilution factor to dilute the extract. This dilution is analyzed by GC/MS for extractable organics.

- If the screen is from the low level preparation, discard the extract and prepare the samples by the medium level method for GC/MS analysis.